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14 YEAR ^{113m}Cd*

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(*Received* 10 *October* 1958)

Abstract—The half-lives of ^{113m}Cd and ^{115m}Cd have been redetermined to be 14 ± 2 years and 44·2 ± 0·5 days, respectively. The ratio of ^{113m}Cd/^{115m}Cd yields from thermal neutron fission of ^{235}U is 0·27 ± 0·03, and the ratio of n, γ formation cross-sections is 0·31 ± 0·03. Combination of these ratios with literature values for the ^{115m}Cd fission yield and n,γ formation cross-section gives (1·9 ± 0·2) × 10^{-4} per cent and 43 ± 10 mbarns for the ^{113m}Cd fission yield and n, γ formation cross-section, respectively.

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WAHL and BONNER[1] reported the formation of a long-lived cadmium isotope, probably ^{113m}Cd, from thermal neutron fission of ^{235}U. A year after the irradiation they observed curvature in the decay curves of the 44 day ^{115m}Cd and showed by repurifying a sample and finding no change in its specific activity that the long-lived component was due to an isotope of cadmium.

The samples have now been followed for an additional seven years on the same methane flow proportional counter.[2] The decay curves have been resolved into 44·2 ± 0·5 day and 14 ± 2 year periods as shown in Fig. 1.

The 44·2 ± 0·5 day value for the ^{115m}Cd half-life is consistent with previously reported values of 43 days[3,4] and 44 days[5] and is probably more precise than these because the contribution of the long-lived tail could be subtracted accurately. For one sample the decay was followed for more than ten half-lives.

The 14 ± 2 year half-life is considerably greater than the 5·1 ± 0·3 year value reported[6] for ^{113m}Cd. Therefore, the mass assignment of the 14 year cadmium isotope was checked in the following ways.

First, in 1955, aluminium absorption curves for the 14 year cadmium from fission and for the long-lived cadmium produced‡ 2 years previously by the n, γ reaction were compared. The curves were identical and had initial half-thicknesses of 19

* This work was done under the auspices of the U.S. Atomic Energy Commission.
† Department of Chemistry, Washington University, St. Louis, Missouri.
‡ The n, γ-produced samples were scraped from a cadmium coated counter of R. E. CARTER and M. E. BUNKER. The counter had been irradiated for about 1 year with thermal neutrons and had not been exposed to neutrons for 2 years. The scrapings were dissolved, purified,[7] and mounted as $CdNH_4PO_4 \cdot H_2O$ on filter paper on aluminium and covered with Scotch Tape, as were the samples produced by fission.[1]

[1] A. C. WAHL and N. A. BONNER, *Phys. Rev.* **85**, 570 (1952).
[2] B. P. BAYHURST and R. J. PRESTWOOD, *Nucleonics* (in press).
[3] L. SEREN, D. ENGELKEMEIR, W. STURM, H. N. FRIEDLANDER and S. TURKEL, *Phys. Rev.* **71**, 409 (1947).
[4] J. M. CORK, W. C. RUTLEDGE, A. E. STODDARD, C. E. BRANYAN and J. M. LEBLANC, *Phys. Rev.* **79**, 938 (1950).
[5] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 895. McGraw-Hill, New York (1951).
[6] W. L. CRASS, J. R. GUM and M. L. POOL, *Phys. Rev.* **80**, 1028 (1950).
[7] *Collected Radiochemical Procedures*, compiled by J. KLEINBERG, Los Alamos Scientific Laboratory Report LA-1721, p. 143 (1954). (Unpublished).

mg/cm², a value that is reasonable[8] for the 0·58 Mev[9,10] β-particles emitted by ^{113m}Cd. The decay of the n, γ-produced cadmium activity has been followed; the half-life is 14 years, as shown in Fig. 1.

Next, normal cadmium and cadmium enriched in ^{112}Cd (83·5 ± 1·0% ^{112}Cd, 4·4 ± 0·5% ^{114}Cd) were irradiated at the same time with thermal neutrons. A year later the samples were purified,[7] mounted,[1] and their decays followed for 2 years. The decay curves were resolved into 44 day and 14 year components. The ratio of

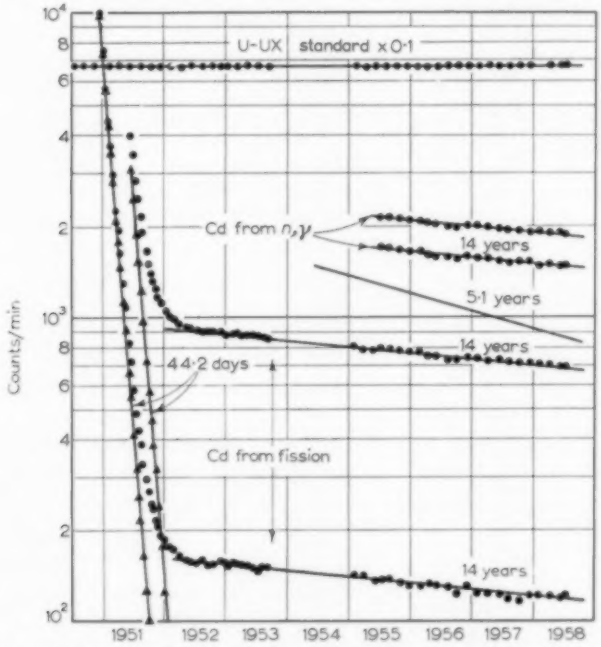

FIG. 1.—Decay curves. ● measured points, ▲ points after subtraction of 14 year tail. Only alternate points are shown.

the 14 year activity to the 44 day activity in the enriched sample was twenty one times this ratio in the normal sample. This factor is the same, within experimental error, as that for the ^{112}Cd/^{114}Cd ratios in the two samples. The samples have not been followed sufficiently long for an accurate half-life determination to be made for the long-lived component. However, the rate of decay, 5 per cent per year, is consistent with a 14 year half-life, but not with a 5·1 year half-life (13 per cent decay per year expected).

It seems clear that the 14 year period is to be assigned to ^{113m}Cd. The reason for the discrepancy between the 14 ± 2 year value and the previously reported[6] 5·1 ± 0·3 year value is not known. Radiochemical impurities, statistical counting fluctuations, instability of the counters, and instability of the samples themselves over the years could cause errors in the values.

[8] D. W. ENGELKEMEIR, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 18. McGraw-Hill, New York (1951).
[9] E. DER MATEOSIAN, *Phys. Rev.* **95**, 646 A (1954).
[10] J. M. CASSIDY, *Phys. Rev.* **83**, 483 A (1951).

The statistical counting fluctuations were small, and the internal consistency of the data reported here were good as shown by least-squares calculations* of the half-life values and their standard deviations; 13·0 ± 0·3 years and 14·7 ± 0·2 years for the samples from fission; 14·5 ± 0·3 years and 14·6 ± 0·4 years for the samples from the n, γ reaction. Because of the discrepancy in values for the fission samples and possible systematic errors, discussed below, the author has chosen 14 ± 2 years as the best value for the half-life.

The counter and associated electronic circuits were quite stable as shown by the constancy of the U–UX standard during the whole of the counting period (0·6 per cent increase during 5·5 years). A ^{204}Tl standard followed since December, 1955 decayed exponentically with a 3·91 ± 0·02 year half-life (least-squares calculation). There were two counter-window changes during 1956 which seemed to alter counting rates slightly (~1 per cent). No correction for this change was attempted.

There is no objective way of determining changes in the samples themselves. The only change observed visually was for the fission samples; the edges of the Scotch Tape covers loosened, and the samples raised slightly. When the edges were taped back down in August, 1956 lowering the samples to their original positions, no change in counting rate was detected. Should the weight of the Scotch Tape cover (original weight 9·2 mg/cm²) have changed 1 mg/cm² the β-intensity penetrating the cover would have changed 3·7 per cent, which would have affected the half-lives of the samples from fission by 17 per cent. There is no evidence that such a change occurred.

The ratio of cross-sections for the reactions ^{112}Cd$(n, \gamma)^{113m}$Cd and ^{114}Cd$(n, \gamma)^{115m}$Cd was calculated to be 0·31 ± 0·03 from the 14 year and 44 day activities in the irradiated normal and enriched cadmium samples. The counting efficiency of ^{113m}Cd relative to the efficiency of ^{115m}Cd was estimated to be 0·50 from the curves of BAYHURST and PRESTWOOD.[2] With the cross-section for the ^{114}Cd$(n, \gamma)^{115m}$Cd reaction taken to be 140 ± 30 mbarns,[11] the cross-section for the ^{112}Cd$(n, \gamma)^{113m}$Cd reaction is 43 ± 10 mbarns. CASSIDY's value,[10] corrected for the change in half-life, is 80 ± 40 mbarns.

The ratio of ^{113m}Cd/^{115m}Cd yields from thermal neutron fission was calculated to be 0·27 ± 0·03. With the fission yield of ^{115m}Cd taken to be $7{\cdot}1 \times 10^{-4}$ per cent,[1] the fission yield of ^{113m}Cd is $(1{\cdot}9 \pm 0{\cdot}2) \times 10^{-4}$ per cent. This is 0·017 of the expected[12] total 113 chain yield. Since the predicted[12,13,14] independent yields of both ^{113}Cd isomers range from (1 to 7) $\times 10^{-5}$ of the total chain yield, most of the ^{113m}Cd in fission must come from β-decay.

Acknowledgements—It is a pleasure to thank Dr. G. A. COWAN, Dr. R. W. SPENCE, and the other members of Group J-11 for their hospitality during the many summers I have spent with them. I wish to acknowledge the assistance of many members of the group, in particular, Mrs. P. NEAL and the other members of the counting group who have counted the samples so faithfully.

* The calculations were programmed by Dr. R. H. MOORE and run by him on the IBM 704 Data Processing Machine.

[11] L. SEREN, H. N. FRIEDLANDER and S. H. TURKEL, *Phys. Rev.* **72**, 888 (1947).
[13] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, pp. 3–14. United Nations, New York (1956).
[12] A. C. PAPPAS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, pp. 19–26. United Nations, New York (1956).
[14] L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 489. McGraw-Hill, New York (1951).

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SEARCH FOR ^{20}O*

S. AMIEL† and R. E. SEGEL‡

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Abstract—An attempt was made to observe ^{20}O by irradiating ^{18}O with tritons produced by the $^{6}Li(n, \alpha)^{3}H$ reaction. Copious quantities of ^{20}F produced by the $^{18}O(t, n)^{20}F$ reaction were observed, but there were no indications of ^{20}O from the $^{18}O(t, p)^{20}O$ reaction. From an analysis of the decay curve and γ-ray spectrum of the irradiated samples, an upper limit of $\tau_{1/2} < 50$ sec for ^{20}O is deduced.

THE great potential utility of a long lived oxygen isotope has prompted several investigators[1,2] to search for ^{20}O. None of these attempts have been successful, a category in which, unfortunately, the experiment reported here must be placed. KATCOFF and HUDIS[1] were able to place the following limits on the half-life: $\tau_{1/2} < 10$ min or $\tau_{1/2} > 150$ years. A half-life of $^{20}O > 150$ years would imply an unreasonably large ^{20}O mass defect and, therefore, a search was undertaken to find this isotope with a half-life in the minutes range.

A likely producer of ^{20}O is the $^{18}O(t, p)^{20}O$ reaction. If the ^{20}O–^{20}F mass difference is sufficiently small for the ^{20}O half-life to be ~minutes, then the Q-value for the $^{18}O(t, p)^{20}O$ reaction should be $> \sim O$[3]. ^{20}O can be expected to decay to ^{20}F, which in turn decays to ^{20}Ne. The ^{20}F decay is exclusively to the 1·65 MeV first excited state of ^{20}Ne, and has a half-life of 11·4 sec[4] (log ft = 4·99). ^{20}O can, therefore, be identified by observing the subsequent ^{20}F decay, even if no strong γ-rays are present following the ^{20}O decay.

EXPERIMENTAL

Samples of LiOH, enriched to 96% ^{6}Li and 89% ^{18}O were placed in highly purified graphite vials and irradiated in the Brookhaven Research Reactor. The ^{18}O was, therefore, bombarded with the tritons which were produced by the $^{6}Li(n, \alpha)H^{3}$ reaction ($Q = 4{\cdot}78$ MeV, $E^{3}_{H} = 2{\cdot}72$ MeV, $\sigma = 930$ barns for thermal neutrons[3]). Short irradiation times (20 sec–2 min) were used, and the sample counting started about 40 sec after bombardment.

The samples were counted by a 3 in. × 3 in. NaI(Tl) scintillation detector, with the resultant spectra displayed on a 100-channel pulse-height analyser. Spectra were taken for 10 sec counts every 20 sec. The spectra were recorded by photographing the cathode ray tube of the analyser, which displays the counts stored in the memory. In this way it was possible to avoid the rather long (2 min) delay in printing out the data.

A typical spectrum is shown in Fig. 1. A strong peak was present at 1·65 MeV, due to the gamma ray following ^{20}F decay. The ^{20}F was made by the $^{18}O(t, n)^{20}F$ reaction, the mirror reaction of the one sought. It is also possible, of course, that some of the ^{20}F came from the decay of ^{20}O. A weak γ-ray at about 1·1 MeV is consistent with, but not definitely established by, the data. This line, if present, decayed at approximately the same rate as the 1·65 line. A weak line was seen at 1·35 MeV,

* Work performed under the auspices of the United States Atomic Energy Commission.

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‡ Guest scientist at Brookhaven National Laboratory, Upton, New York. Address: Aeronautical Research Laboratory, Dayton, Ohio.

[1] S. KATCOFF and J. HUDIS, *J. Inorg. Nucl. Chem.* **3**, 253 (1956).
[2] R. K. SHELINE, E. C. CAMPBELL and R. W. PEELE, ORNL-1798 (1954). Unpublished.
[3] F. AJZENBERG and T. LAURITSEN, *Rev. Mod. Phys.* **27**, 77 (1955).
[4] C. WONG, *Phys. Rev.* **95**, 765 (1954).

which decayed with a significantly longer half-life than the 1·65 line. This γ-ray was probably due to ^{19}O (30 sec). A line at about 500 keV appeared to grow into the spectrum. This γ-ray could not have been connected with the ^{20}O–^{20}F–^{20}Ne decay chain as it remained long after the 1·65 MeV γ-ray had decayed away. If ^{20}O was present at the time the samples were counted either ^{20}O must be predominantly a pure β-emitter, or, perhaps emit a γ-ray of energy about 1·65 MeV.

Graphite vials containing $^{6}LiOH$ made from normal water were irradiated and counted in order to check that the spectra observed were really due to reaction with ^{18}O. The counting rate with these samples was lower by several orders of magnitude from the samples containing the enriched oxygen.

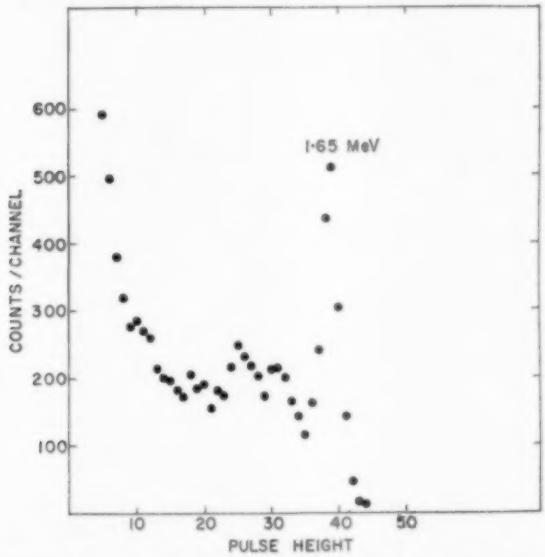

FIG. 1.—Spectrum observed in NaI(Tl) crystal 1 min after bombardment. The counter was calibrated with radioactive sources which emit γ-rays of known energy.

Simultaneously to the spectral measurements, a decay curve was taken of the output of a single channel analyser biased to accept pulses between 1·55 and 1·75 MeV. One of these decay curves is shown in Fig. 2. The decay appears to have a single component, of half-life 13·5 sec. This is somewhat higher than, but consistent with, the 11·4 sec half-life measured by WONG[4] for ^{20}F. About 1 mc of ^{20}F seems to have been produced.

DISCUSSION

From the amount of ^{20}F produced, it is possible to estimate how much ^{20}O must have been made. One would expect a greater ^{20}F production because:

(1) The greater level density in ^{20}F.

(2) The higher Q value for the $^{18}O(t, n)^{20}F$ ($Q = 6{\cdot}1$ MeV) reaction relative to that for the $^{18}O(t, p)^{20}O$ reaction.

(3) A coulomb barrier inhibition of the outgoing proton in the (t, p) reaction.

If one assumes $Q = -0{\cdot}5$ MeV, which is the value calculated from the mass defect estimated by SHELINE *et al.*[5] then one would expect the ^{20}O production to be a few per cent of the ^{20}F production. Assuming the ^{20}O production to be 1 per cent of the ^{20}F production, then the decay curve measured here puts an upper limit of $\tau_{1/2} < 30$ sec for ^{20}O. If the more pessimistic assumption is made that only 0·1 per cent as

[5] R. K. SHELINE, N. R. JOHNSON, P. R. BELL, R. C. DAVIS and F. K. MCGOWAN, *Phys. Rev.* **94**, 1642 (1954).

much ^{20}O as ^{20}P was produced, than an upper limit of $\tau_{1/2} < 50$ sec can be deduced from the data.

The ^{20}O–^{20}F mass difference and the ^{20}O half-life can, of course, be correlated. If one assumes the same log ft = 5 for an allowed β-transition in the ^{20}O decay as is measured for the ^{20}F decay, then in order for $\tau_{1/2} > 50$ sec we must have $E_\beta < 4{\cdot}0$ MeV. If the decay to any one of the first six states in ^{20}F were allowed, then the ^{20}O–^{20}F mass difference should be $<5{\cdot}4$ MeV. This would imply $Q > 1{\cdot}5$ MeV for the $^{18}O(t, p)^{20}O$ reaction, in which case there should have been a few per cent ^{20}O produced relative

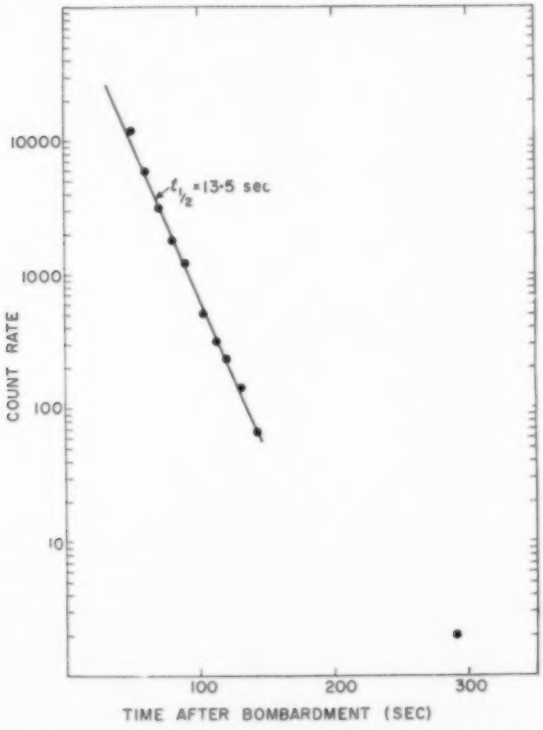

FIG. 2.—Counting rate vs. time for pulses between 1·55 and 1·75 MeV. The counting rate is in arbitrary units.

to the ^{20}F production. An upper limit of $\tau_{1/2} < 50$ sec for the ^{20}O decay appears, therefore, to be a reasonable conclusion from the experiment reported here. In fact, a $\tau_{1/2} < 30$ sec seems most probable.

Finally, we must consider the possibility that ^{20}O is relatively long lived. Should this be the case, a relatively small ^{20}O–^{20}F mass difference is implied and, therefore, a higher Q for the $^{18}O(t, p)^{20}O$ reaction. In this eventuality, the reasons given above for the inhibition of the ^{20}O production relative to that of the ^{20}F would no longer be as severe and we can assume that a lower limit of 5 per cent for the ^{20}O production relative to that of the ^{20}F production is quite safe. The sensitivity of the present experiment would then be limited by the ratio of the irradiation time (20 sec) to the ^{20}O half-life. Postulating a long-lived ^{20}O the data in Fig. 2 yield an upper limit

of 2×10^{-4} ^{20}O activity relative to ^{20}F activity at the end of the neutron bombardment. Combining this with the assumed 5 per cent ^{20}O production a lower limit for the ^{20}O half-life of $\tau_{1/2} > 5{,}000$ sec (80 min) is deduced. This upper limit well overlaps the lower limit of $\tau_{1/2} < 10$ min found by KATCOFF and HUDIS.[1]

It should be noted that these results are in conflict with a half-life of 3_{-2}^{+8} min predicted by THIEBERGER.[6]

From the results reported here, the conclusion must be drawn that an oxygen isotope longer lived than ^{15}O (2 min) does not appear to exist.

Acknowledgements—The authors wish to acknowledge the encouragement and helpful suggestions of Mr. L. STANG during the early phases of this work. Thanks are also due to Dr. W. S. GINELL for purifying the graphite vials and to Mr. A. WEISS for his assistance in taking some of the data.

[6] R. THIEBERGER, *J. Inorg. Nucl. Chem.* **4**, 367 (1957).

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DISSOCIATION OF TH AND T_2 BY β-DECAY*

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Abstract—The positively charged fragments resulting from β-decay in the diatomic molecules TH and T_2 were analysed by the techniques of mass spectrometry. The data on tritium hydride support the findings of SNELL *et al.*[1] that the $(HHe^3)^+$ daughter usually remains bound in the nuclear transformations. The stability against dissociation of the ionized daughter molecules [$(HHe^3)^+$ and $(THe^3)^+$] was observed to depend slightly on the mass of the bonding partner. The results are discussed within the framework of the Franck–Condon principle.

IN β-emission the decay electron leaves the emitting atom in a time which is short relative to periods of electronic and (especially) atomic motion. If the emitter is one of the partners of a diatomic molecule, the motions of the atoms during the nuclear transformation are consequently negligible; and changes in molecular states accompanying β-decay may be considered as transitions from the ground electronic level of the parent molecule to the ground or excited states of the daughter molecule, these transitions taking place in accordance with the Franck–Condon principle. Excited electronic states of the product become accessible because of the perturbation of the electrostatic environment of the electronic cloud by the sudden change of nuclear charge.[2]

Whether or not an ionized daughter diatomic molecule, formed as a result of the increase in nuclear charge in a negative β-emission, dissociates depends on whether a repulsive daughter state or a vibrational level higher than the dissociation limit of a bound daughter electronic state is reached in the particular vertical transition associated with the β-decay. An excited molecule-ion which survives dissociation in the initial nuclear transformation may still break apart in subsequent radiative or predissociative transitions. Added to these mechanisms of molecular rupture is that of recoil from the β-particle. Thus when one of the atoms undergoes β-decay, even the behaviour of a simple diatomic molecule may be complex, and in the present state of theory a detailed treatment of the problem is formidable. CANTWELL[3a] has calculated transition probabilities from the electronic ground states of TH and T_2 to several vibrational levels of the lowest states of their daughters. WOLFSBERG[3b] has also considered theoretically some aspects of β-decay in molecules.

An experimental approach to the study of the behaviour of diatomic molecules in β-decay, which is reported here, uses the mass spectrometric techniques previously employed in the charge and mass analysis of rare gas atoms and molecules undergoing nuclear decay.[4,5] Specificially, the ionic fragments arising from β-emission in the

*Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] A. H. SNELL, F. PLEASONTON and H. E. LEMING, *J. Inorg. Nucl. Chem.* **5**, 112 (1957).
[2a] A. MIGDAL *J. Phys.* (*U.S.S.R.*) **4**, 449 (1941); [b]E. L. FEINBERG, *Ibid.* **4**, 423 (1941); [c]A. WINTHER, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **27**, No. 2 (1952).
[3a] M. CANTWELL, *Phys. Rev.* **101**, 1747 (1956); [b] M. WOLFSBERG, *J. Chem. Phys.* **24**, 24 (1956).
[4] A. H. SNELL and F. PLEASONTON, *Phys. Rev.* **107**, 740 (1957) and earlier papers.
[5] S. WEXLER and D. C. HESS, *J. Phys. Chem.* **62**, 1382 (1958).

isolated molecules TH and T_2 were observed in a mass spectrometer with special constructional features. Thereby the effect of the mass of the bonding partner on the stability of the daughter molecule-ion against dissociation could be appraised in a pair for which corresponding electronic interaction curves should be identical to a high approximation.[6] A fragmentation pattern of the tritium hydride molecule in β-decay has already been published.[1] Since the data were taken in a spectrometer of considerably different ion optics from the one described in this paper, a comparison of the patterns should reveal any serious mass discriminatory effects of the experimental arrangements.

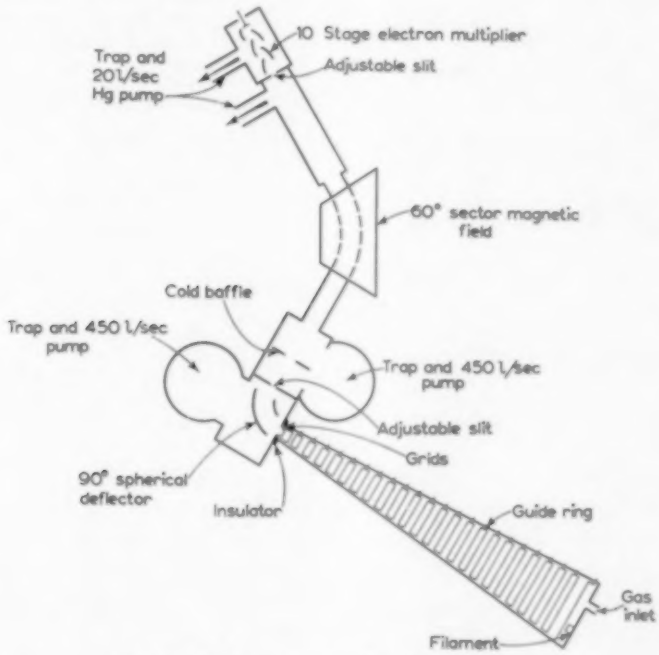

FIG. 1.—Mass spectrometer for radioactive gases.

I. EXPERIMENTAL

A profile sketch of the mass spectrometer appears in Fig. 1. The radioactive TH and T_2 were introduced separately through a capillary leak into the conical source volume (80 l. in volume), and decayed there at a pressure which varied between 3 and 14×10^{-6} mm. The positive ions formed as a result of the β-transition were urged toward the apex of the cone by an electric field produced in the source volume by applying proper potentials to the series of guide rings within the conical housing. A total potential difference of 500 V was impressed across the ring system. The energies of the ionic decay products were then increased to 6500 V as they passed between two grids of high transmission near the vertex of the cone. The positively ionized fragments were separated from the neutral molecules exuding from the source by a 90° spherical electrostatic deflector of 3 in. mean radius. The ions then passed through an adjustable slit and the mass analysis was performed by deflecting them magnetically through 60° on a circle of 12 in. radius. The field was monitored by a rotating fluxmeter. The fragments were detected by a ten-stage Dumont electron multiplier (No. 6292) prepared and operated according to the directions of KOYOMA and CONNALLY,[7] but shielded against

[6] G. HERZBERG, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (2nd Ed.) p. 162. Van Nostrand, New York (1950).
[7] K. KOYOMA and R. E. CONNALLY, *Rev. Sci. Instrum.* **28**, 833 (1957).

stray magnetic fields. The elaborate pumping system was necessary to prevent the radioactive gases from diffusing into the detector chamber and decaying there, thereby causing a prohibitively high background. Intensities of the ions were high, ranging from 1000 to 180,000 counts per min, depending on the fragment and the pressure of active gas in the source. However, the background of the detector increased as the experiment progressed, so that measurements on fragments of very low intensity, such as $(He^3)^{++}$ (see below), could not be made.

Tritium hydride gas containing only 0·4 per cent of T_2 was synthesized by reaction of T_2O on an outgassed slurry of $LiAlH_4$ in *n*-butyl ether at 0°C. The procedure was similar to that described by WENDER *et al.*,[6] but omitted their use of a carrier gas. The sample of molecular tritium was taken from a supply available at this laboratory. Analysis showed the T_2 gas to contain 11·5% TH.

II. RESULTS

Relative intensities found for the various fragments from β-decay in the molecules TH and T_2, respectively, are presented in Table 1. Correction for an impurity of TH has been made in the results on T_2. Corrections for counting losses have been made

TABLE 1.—DISSOCIATION OF TH AND TT BY β-DECAY

Molecule	Ion fragment	Probability of occurrence (%)	
		This work	SNELL *et al.*[1]
TH	$(He^3H)^+$	89·5 ± 1·1	93·2 ± 1·9
	$(He^3)^+$	8·2 ± 1·0	5·1 ± 0·3
	H^+	2·3 ± 0·4	1·55 ± 0·16
	$(He^3)^{++}$		0·14 ± 0·01
TT	$(THe^3)^+$	94·5 ± 0·6	
	$T^+ + (He^3)^+$	5·5 ± 0·6	

also. Errors listed are standard deviations, and take into account statistics of counting, reproducibility of the intensity measurements, and inaccuracies in the corrections for variation of multiplier efficiency for the different ions.

Included, for comparison, are the results of SNELL *et al.*[1] on tritium hydride. It is seen that the data are in reasonable agreement, despite the great difference in ion optics in the two mass spectrometers and the corrections which the use of an equilibrium mixture of TH, T_2, and H_2 necessitated in the earlier work. The ionized helium hydride molecule appears to show a strong tendency to remain bound, at least for its transit time through the spectrometer (about 10^{-4} sec), despite the many ways it can dissociate. When the ion does break up, it apparently does so by two separate modes:—

$$(HHe^3)^+ \rightarrow (He^3)^+ + H \quad (1)$$

$$(HHe^3)^+ \rightarrow He^3 + H^+ \quad (2)$$

The mechanism which involves one electron going with each fragment apparently predominates, as indicated by the higher yield of the $(He^3)^+$ over that of H^+. An upper limit of the probability of orbital ionization accompanying β-decay is given by

[6] I. WENDER, R. A. FREIDEL and M. ORCHIN, *J. Amer. Chem. Soc.* **71**, 1140 (1949); M. ORCHIN and I. WENDER, *Analyt. Chem.* **21**, 875 (1949).

the sum of the ion yield of $(H)^+$ plus that of $(He^3)^{++}$ since the two modes of rupture of $(HHe^3)^{++}$ are

$$(HHe^3)^{++} \rightarrow H^+ + (He^3)^+ \quad (3a)$$

and

$$(HHe^3)^{++} \rightarrow H + (He^3)^{++} \quad (3b)$$

The probability of 1·7 to 2·3 per cent found may be compared with the theoretical value of 2·5 per cent for the probability of ejection of the single electron in the transformation of atomic tritium to helium-3 ion.[2a] This may also be compared with WINTHER's[2c] calculated value of 10·5 per cent for the probability of orbital electron ionization following β-decay in He^6.

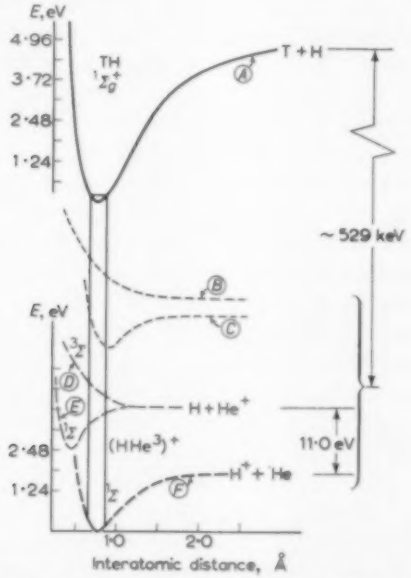

FIG. 2.—Potential energy curves for the ground state of (TH) and for several states of $(HHe^3)^+$.

Table 1 also contains the observations on molecular tritium. Here the resolution of the spectrometer is much too poor to distinguish between T^+ and $(He^3)^+$. One notes that the helium tritide ion appears to be less susceptible to dissociation than the ionized helium hydride molecule. The difference in ion yields (Table 1) found is 5·0 per cent with an error (standard deviation) estimated to be 1·3 per cent.

III. DISCUSSION

As pointed out in the Introduction, the molecular changes caused by β-decay of atoms in diatomic (as well as polyatomic) molecules may be discussed in terms of Franck–Condon transitions because the movements of the nuclei are very slow relative to the motions of the electrons and decay particles. Such transitions may be illustrated by use of the electronic interaction-potential curves shown in Fig. 2. The potential curve for the ground state of the TH or TT molecule (curve *A*) is very nearly identical[6] to that for molecular hydrogen,[9] and the curve of energy vs. internuclear

[9] G. HERZBERG, *Molecular Spectra and Molecular Structure* (2nd Ed.) p. 99. Van Nostrand, New York (1950).

distance for the ground state of the $(HHe^3)^+$ or $(THe^3)^+$ ion (curve *F*) is taken from EVETT's calculations.[10] Also shown are the forms of the functions for the first two excited states of the molecule-ion (curves *D* and *E*).[11] An effort was made to draw the curves to the same scale and in their proper positions relative to each other. The curve of the TH or TT molecule is some 529 keV (the energy of the nuclear transition) above the others. Finally, to aid in the discussion which follows, two additional curves (*B* and *C*) were drawn to illustrate possible excited levels for which no information is available.

The changes in the molecular system which take place by virtue of the beta emission are limited by the Franck–Condon principle to vertical transitions within the two heavy vertical lines on Fig. 2. Since essentially all the TH molecules are in their lowest vibrational level at room temperature,[12] the beta transformation involves a change from this level to various vibrational levels of the several electronic states accessible. In addition to molecular transitions to the ground state of the $(HHe^3)^+$, there are finite probabilities for transitions to excited electronic levels of the daughter ion.[2] These are the result of the "shaking" of the atomic core as a result of the sudden change of nuclear charge. Because the β-particle is ejected in a time very small relative to periods of orbital electron motion, a sudden perturbation in the electrostatic environment of the electrons occurs, as the electrons now feel the electric field produced by the new nuclear charge. In most of the negative β-transformations there will be an adiabatic shrinkage of the atomic core to accommodate to the new field. In these there will be no electronic excitation. But sometimes there are large probabilities for non-adiabatic transitions, i.e. excitations and ionizations.

Excited $(HHe^3)^+$ ions will eventually degrade in energy in one or more steps to the ground state or a metastable state with emission of radiation. While radiative lifetimes are of the order of 10^{-8} sec, the transit times of the ions in the source cone of the spectrometer are about 10^{-4} sec; consequently, the ions observed in this experiment will be those in their electronic ground state or in excited metastable levels. However, the time for one vibration of the ionized diatomic molecule is only of the order of 10^{-14} sec. Thus a Franck–Condon transition to a vibrational level above the dissociation limit of a particular electronic state will result in immediate rupture of the ion, and only atomic ions will be observed from these transitions. Dissociation can occur either in a molecular transition accompanying the β-emission or, later in time, as the result of a radiative or pre-dissociation transition from excited electronic states reached initially, or from intermediate levels formed in the de-excitation process. In some dissociations charged He^3 and neutral H are formed while in others both bonding electrons go with the helium-3, so that charged hydrogen appears. The experimental yields of $(He^3)^+$ and H^+ are therefore the net result of numerous different dissociative transitions in the molecular system. That the helium ion is found to be more abundant than H^+ is a chance result of several factors such as the relative probabilities of the many molecular transitions accompanying the beta emission, the kind of state reached, the repulsive or bound character of this state, the relative positions of the many potential curves, and the relative probabilities of

[10] A. A. EVETT, *J. Chem. Phys.* **24**, 150 (1956).
[11] J. A. CRAWFORD, Berkeley Astronomical Dept., University of California, Private communication, May, 1958.
[12] G. HERZBERG, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (2nd Ed.) p.123. Van Nostrand, New York (1950).

the possible radiative transitions. Study of Fig. 2 will make apparent some of the possible molecular transitions which beta transformation may initiate in the TH—$(HHe^3)^+$ system. One may conclude from the diagram that atomic ions can eventually arise only from β-transitions to excited states of $(HHe^3)^+$ more than 11 eV above the ground level.

The experimentally observed ion yield of 90 per cent or more for the two ionized molecules suggests that the bulk of the transitions are to the bound ground state of $(HHe^3)^+$ or $(THe^3)^+$ and/or that nearly all excited levels reached in the β-emission, or by subsequent radiation, are also attractive. However, this value of the yield may be considered as only an upper limit for the tendency of $(HHe^3)^+$ or $(THe^3)^+$ ions to remain bound for at least 10^{-4} sec. Fig. 2 reveals that Franck–Condon transitions to repulsive states or repulsive parts of bound states of the ionized molecule are possible. Such ions would dissociate in one vibration, the fragments flying apart with considerable kinetic energy.[13] Since mass spectrometers strongly discriminate against ions with appreciable translational energy,[14] the measured yields of the atomic fragments would be too low and, accordingly, that of the bound molecular ion too high. Perhaps a contributing factor is a quantum mechanical selection rule, applicable to molecular transitions accompanying β-decay, according to which the total, orbital, and spin angular momenta of a molecular system must individually remain unchanged in beta emission.[15] For the diatomic system under consideration, then, only $^1\Sigma \rightarrow {}^1\Sigma$ transitions are allowed. As seen in Fig. 2, the ground and first excited states of $(HHe^3)^+$ are singlet states and bound; transitions to these levels would result in ions of low kinetic energy. But higher $^1\Sigma$ excited states of the ionized molecule may be repulsive, and transitions to these would give rise to atomic ions of high translational energy.[13] Taking the results of calculations on atomic tritium as a guide, one may expect molecular transitions to states rather high in energy above the ground state. From MIGDAL's[2a] equations one obtains a distribution of $(He^3)^+$ states which decreases rapidly with the energy of excitation following β-decay of T. In this calculation 70 per cent of the $(He^3)^+$ ions are formed with no excitation, 25 per cent with 40·8 eV, and 2·5 per cent with energies between 40·8 and 54·1 eV; 2·5 per cent of the daughters possess electronic excitations in excess of the ionization potential of $(He^3)^+$. Many accessible levels of $(HHe^3)^+$ or $(THe^3)^+$ would be expected in this energy range if H_2 is considered a suitable analogue.[16]

On the other hand, the relative abundances reported here for the fragments from TH agree reasonably well with those observed by SNELL *et al.*,[1] despite the great differences in experimental conditions. This may suggest that variations in energy among the fragments formed in this β-transformation are not large. But it is interesting to note that the ion yields of both H^+ and $(He^3)^+$ are higher in the experiment reported here. Apparently, our experimental conditions possess a higher efficiency of collection for these ions relative to the molecule-ion than those of the previous study. Such variations, which depend on ion optics, would be expected if

[13] See, for example, the results of H. D. HAGSTRUM, JR., *Rev. Mod. Phys.* **23**, 196 (1951), the calculations of EVETT[10] on the first repulsive state of $(HHe)^+$, and W. DE GROOT and F. M. PENNING, *Handb. d. Physik* **23** (1), 114 (1933).

[14] An extensive study of discrimination effects has been done by C. E. BERRY, *Phys. Rev.* **78**, 597 (1950).

[15] H. M. SCHWARTZ, *J. Chem. Phys.* **21**, 45 (1953).

[16] G. HERZBERG, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (2nd Ed.) p. 530. Van Nostrand, New York (1950); W. DE GROOT and F. M. PENNING, *Handb. d. Physik* **23** (1), 114 (1933).

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the initial kinetic energies of the atomic ions differed from that of the charged molecule.

A lower limit to the tendency to form bound molecule-ions may be derived from theoretical calculations of the probability of transitions from the electronic ground level of TH to the ground state of $(HHe^3)^+$. CANTWELL[3] estimates this value to be 58 per cent, which is believed to be a more accurate value than SCHWARTZ's[15] 71 per cent. Since EVETT[10] has shown the ground state of the helium hydride ion to be bound and its equilibrium internuclear distance to be near that of TH, transitions directly to this level (Fig. 2) will yield bound ions. As a matter of interest, 55 per cent out of the 58 per cent computed by CANTWELL is the sum of transition probabilities to the lowest three vibrational levels of the ionized daughter molecule. These levels should be well below the dissociation limit of the $(HHe^3)^+$ ion.

Comparison of the ion yields (Table 1) of $(HHe^3)^+$ and $(THe^3)^+$ shows that the molecule with the heavier isotope appears to be slightly less susceptible to dissociation as a result of beta decay. A difference in the direction observed is expected from the slight difference in zero-point energies of the TH and T_2 molecules. Since the reduced mass of TH is smaller than that of T_2, its zero-point vibrational energy is larger, and consequently, tritium hydride has the greater effective amplitude of vibration. Because of this, Franck–Condon transitions to vibrational levels above the dissociation limit are more possible following β-decay in TH than in T_2. This is illustrated in Fig. 2 by molecular transitions from curve *A* to the sharply rising portion of curve *C*. A slight variation in zero-point energy [the difference in $(E_0)_{v1b}$ of the two molecules is only 0·07 eV] of the parent molecule will cause a marked change in the number of transitions which yield atomic ions. Accordingly, the difference in yields of the molecule-ions is in the proper sense, but a critical comparison with theory is not possible at present because of a lack of knowledge about the potential curves of the states involved. It is of interest in this connection that similar mass effects have been observed in electron impact on the isotopic molecules H_2, D_2 and T_2.[17] The discussion here follows the explanation offered for the isotope effect on dissociation following ionization by electron impact.[18]

With the exception of CANTWELL's calculations, the discussion thus far has ignored the contribution of recoil from the β-emission to dissociation of the daughter molecule-ion. The maximum amount of internal energy $(E_{i,r})$ which the recoil from the β-emission makes available for bond rupture in a diatomic molecule is given by[19]

$$(E_{i,r})_{\max} = \frac{W_\beta^2 - M_\beta^2}{2M_1}\left(1 - \frac{M_1}{M_1 + M_2}\right). \tag{4}$$

Here W_β and M_β are the total and rest energies of the β-particle, M_1 the mass of the daughter atom after β-decay, and M_2 the mass of the bonding partner (all in energy units). The first factor in equation (4) represents the total recoil energy (assuming the emitting atom suffers the entire recoil initially) and the term in parentheses is the correction for translational motion of the molecule. With the aid of the schematic

[17] O. A. SCHAEFFER and J. M. HASTINGS, *J. Chem. Phys.* **18**, 1048 (1950).
[18] O. A. SCHAEFFER and J. M. HASTINGS, *J. Chem. Phys.* **18**, 1048 (1950); D. P. STEVENSON, *J. Chem. Phys.* **15**, 409 (1947); W. BLEAKNEY, E. U. CONDON and L. G. SMITH, *J. Phys. Chem.* **41**, 197 (1937).
[19] J. E. MONAHAN, *Argonne National Laboratory, Physics Division Summary Report*, September (1958). A similar relation derived non-relativistically has been given by H. SUESS, *Z. Physik Chem.* B **45**, 312 (1940).

plot in Fig. 3, one may show the manner by which the internal energy from recoil adds to the vibrational energy the ionized daughter molecule obtains as a result of the Franck–Condon transition. In this figure n_1 is the lowest vibrational level of the TH or T_2 electronic ground state, with dissociation energy D_0, n' a vibrational level of an electronic state of $(HHe^3)^+$ or $(THe^3)^+$ reached in the vertical transition, and n_f the final level actually attained because of recoil. If the sum of the two energies exceeds the dissociation energy D_0' of the particular electronic state, the molecule-ion will of course dissociate. In the illustrated case (Fig. 3) recoil causes dissociation of the molecule-ion which otherwise would have remained bound.

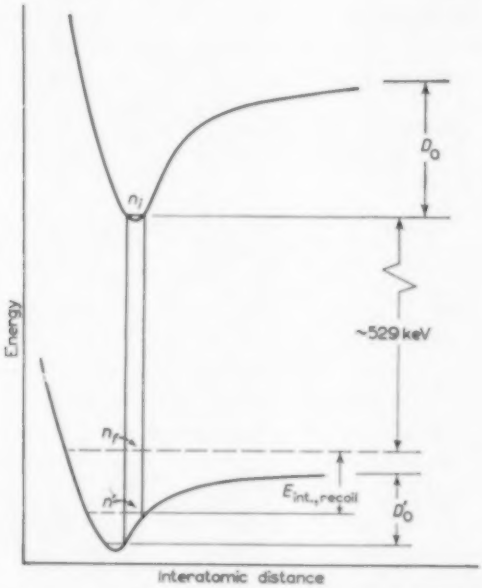

FIG. 3.—Schematic energy diagram to illustrate effect of recoil from beta emission on dissociation of daughter molecule-ion.

Quantitative conclusions about the effect of recoil on the dissociation of $(HHe^3)^+$ and $(THe^3)^+$ are at present possible only for those ions formed in β-transitions to the lowest vibrational level of the electronic ground state. The dissociation energy of the ground state is estimated by EVETT[10] to lie between 1·75 and 2·05 eV for both ionized molecules. Since the maximum recoil energy is 3·6 eV, $E_{i,r}$ for $(HHe^3)^+$ and $(THe^3)^+$ is, from Eq. (4), 0·9 and 1·8 eV, respectively. Thus the condition for dissociation of the molecule is not attained, in this special case, for $(HHe^3)^+$, and possibly not for $(THe^3)^+$, even when the available energy is a maximum. Furthermore, taking into account the energy spectrum of the β-rays from tritium,[20] one may conclude that 92 per cent of the recoil energies lie below 2·0 eV. Accordingly, in this percentage of the transitions, the energy available for bond rupture is less than 0·5 eV in $(HHe^3)^+$ and less than 1·0 eV in $(THe^3)^+$. The internal energy from recoil will exceed 1·5 eV in only 1 per cent of the β-transformations to $(THe^3)^+$. Because the

[20] E. P. COOPER and F. T. ROGERS, JR., *Phys. Rev.* **77**, 402 (1950).

total energy of the nuclear transition from tritium to helium-3 is so low (529 keV), the recoil from the neutrino is negligible. At most this energy amounts to 0·06 eV.

In conclusion, it is highly unlikely that recoil will cause break-up of these molecule-ions when they are formed in the zero vibrational level of the ground state. But the daughter molecules formed by vertical transitions to sufficiently high vibrational levels of the electronic ground state or excited states may dissociate by this mechanism, whereas in the absence of recoil they would remain bound. If the recoil energy is large enough to cause bond rupture when the vertical transition is to an excited vibrational state of the ground electronic state, one would expect that the probability of the dissociation of the daughter $(THe^3)^+$ would exceed that of $(HHe^3)^+$ because of the more efficient transfer of recoil energy to $(THe^3)^+$. Since, on the contrary, dissociation of $(HHe^3)^+$ was actually more probable, the effect of recoil energy must be less important than the relative zero-point energies of TH and TT.

Acknowledgement—The author wishes to thank Drs. J. E. MONAHAN and R. L. PLATZMAN for illuminating discussions on theoretical aspects of the work.

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BRANCHING FRACTION AND HALF-LIFE OF POTASSIUM-42

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Abstract—Measurements have been carried out to determine the branching fraction and half-life of potassium-42. A value of 0·184 ± 0·014 for the number of 1·51 MeV photons/dis was obtained by absolute counting and ionization chamber techniques. The half-life measurements yielded a value of 12·37 ± 0·09 hr.

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THE extensive use of the nuclide ^{42}K at this laboratory as a radioactive standard and tracer made necessary a more accurate knowledge of certain features of its decay scheme. ^{42}K decays to the ground state of ^{42}Ca by emission of either a 3·6 MeV β-particle or a 2·1 MeV β-particle followed by a 1·51 MeV γ-ray. The branching fraction for this type of decay may be defined simply as

$$\alpha = N_\gamma / N_\beta \tag{1}$$

where N_γ = rate of emission of γ-photons, N_β = rate of emission of β-particles.

Measurement of the total disintegration rate by absolute β-counting and the γ-ray emission rate by ionization chamber techniques provide the primary data required for calculation of the branching fraction. N_γ is obtained from ionization chamber measurements by

(1) a knowledge of the efficiency, E_γ, of the ionization chamber for 1·51 MeV photons,
(2) the composite efficiency, E_β, of the chamber for bremsstrahlung production from 3·6 and 2·1 MeV β-particles and
(3) the reasonable assumption that internal conversion will be very low.

If I_γ is the total observed ionization current corrected for background then

$$I_\gamma = N_\gamma E_\gamma + N_\beta E_\beta \tag{2}$$

where the last term defines the ionization current from bremsstrahlung production. By substitution, equation (1) becomes

$$\alpha = I_\gamma / N_\beta E_\gamma - E_\beta / E_\gamma. \tag{3}$$

E_γ at 1·51 MeV for the 4π-ionization chamber was determined from a response curve[1,2] based on measurements made on a series of γ-emitting nuclides. For each nuclide a given solution was measured in a reproducible geometry in the ionization chamber and the absolute disintegration rate for the same sample was determined

[1] C. F. MILLER, USNRDL-TR-155 (1957).
[2] D. LOVE and J. MACKIN, USNRDL, Unpublished data.

independently. The efficiency of the chamber for that nuclide in milliamperes per disintegration per minute (mA/dis/min) thus obtained was then converted, using the nuclide decay scheme, to an efficiency, E_γ, in mAs/photon/min at the particular energy. The instrument used in this study was essentially the same as that described by JONES and OVERMAN[3] consisting of a large steel chamber filled with argon gas at approximately 40 atmospheres.

E_β as a function of beta energy was determined in a similar manner using standard solutions of pure β-emitters under identical conditions. The bremsstrahlung response curve construction was parallel to methods employed by TOMPKINS *et al.*[4] who used a similar ionization chamber for estimation of β-activities. The method of calculation of E_β for ^{42}K required extrapolation of the bremsstrahlung response curve to 3·6 MeV. Since two β-branches are involved an apparent branching fraction was calculated using only the first term of equation (3). From the value thus obtained the efficiencies for the 2·2 and 3·6 MeV branches were read from the response curve and the weighted average used in application of equation (3) for all determinations of α. Under the experimental conditions employed in this study the ionization current produced by bremsstrahlung represented approximately 10 per cent of the total observed ionization current, I_γ. The value obtained for E_β was in good agreement with theoretical calculations based on application of the HEITLER theory[5] as described by WYARD.[6]

TABLE 1.—COMPARISON OF BRANCHING FRACTION WITH METHOD FOR DETERMINATION OF N_β

Sample no.	α	Method for determination of N_β
1	0·1904	proportional
2	0·1757	proportional
3	0·1789	4π
4	0·1797	proportional
5	0·1886	4π
6	0·1860	NBS
7	0·1886	4π
8	0·1852	proportional
9	0·1850	NBS
10	0·1824	proportional
Mean	0·184 ± 0·014	

Determinations of N_β were made on aliquots of the solutions used for the ionization chamber measurements. The disintegration rates were obtained by 4π absolute β-counting or by counting with proportional β-counters previously standardized with ^{42}K. For two of the solutions measured the calculations were made on the basis of disintegration rates provided by the National Bureau of Standards.

Table 1 lists the value of α obtained from a number of measurements made over

[3] J. W. JONES and R. T. OVERMAN, U.S.A.E.C. ORNL-2367 (1948).
[4] P. C. TOMPKINS, L. WISH and W. T. BURNETT, JR., *Analyt. Chem.* **22**, 672 (1950).
[5] W. HEITLER, *The Quantum Theory of Radiation*. Oxford University Press, London (1944).
[6] S. J. WYARD, *Nucleonics* **13**, 44 (1955).

a period of approximately one and one-half years. Since only the method for determination of N_β was varied the particular method employed is also shown. The solutions with the exception of Sample No. 10 were used as obtained from either Oak Ridge National Laboratory or the National Bureau of Standards.

In order to check for significant γ-activities other than ^{42}K γ-ray spectra and half-life measurements were routinely made on aliquots of the standard solutions.

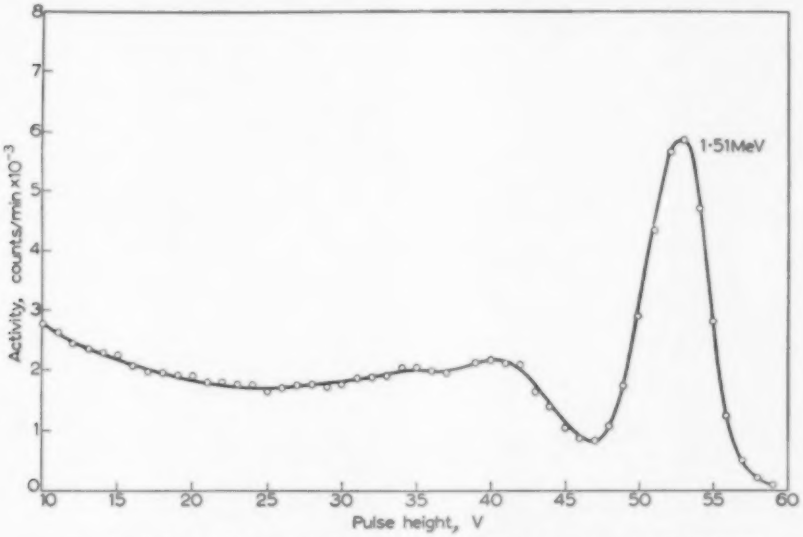

FIG. 1.—Pulse height spectrum for potassium-42 [^{42}K spectrum crystal–3″ NaI(TL)].

Fig. 1 presents a typical spectrum from a 3 in. NaI(Tl) crystal and pulse height analyser. No peaks other than the 1·51 MeV were evident. As a further check on the effect of impurities the solution used in measurement 10 (Table 1) was scavenged with iron hydroxide, evaporated to dryness twice, dissolved in 0·7 N HCl and placed on a Dowex-50 (colloidal, 400 mesh) ion exchange column. The activity was then eluted with 0·7 N HCl according to the method of Beukenkamp and Rieman for the ion exchange separation of Na and K.[7] No activity peaks other than potassium were noted although only the fractions taken at the peak were collected for measurement. The value for the branching fraction (No. 10 in Table 1) on this sample was within both the precision and the estimated accuracy of the measurements.

Routine checks on the half-life of ^{42}K at this laboratory using aliquots of the solutions listed in Table 1 have generally yielded values varying from 12·3 to 12·6 hr depending upon the number of observations and the instrument used. In some cases when prolonged measurements were taken a relatively long-lived impurity was evident which represented a small fraction of the total initial activity. To determine the effect of possible impurities on the measured half-life value portions of Sample No. 10 which had been chemically treated as described above were prepared for β-counting. By preparing samples representing various multiples of activity and by overlapping the decay curves it was possible to extend the measurements over a long period. The composite decay curve is shown in Fig. 2. The activity of the relatively

[7] J. BEUKENKAMP and W. RIEMAN, *Analyt. Chem.* **22**, 582 (1950).

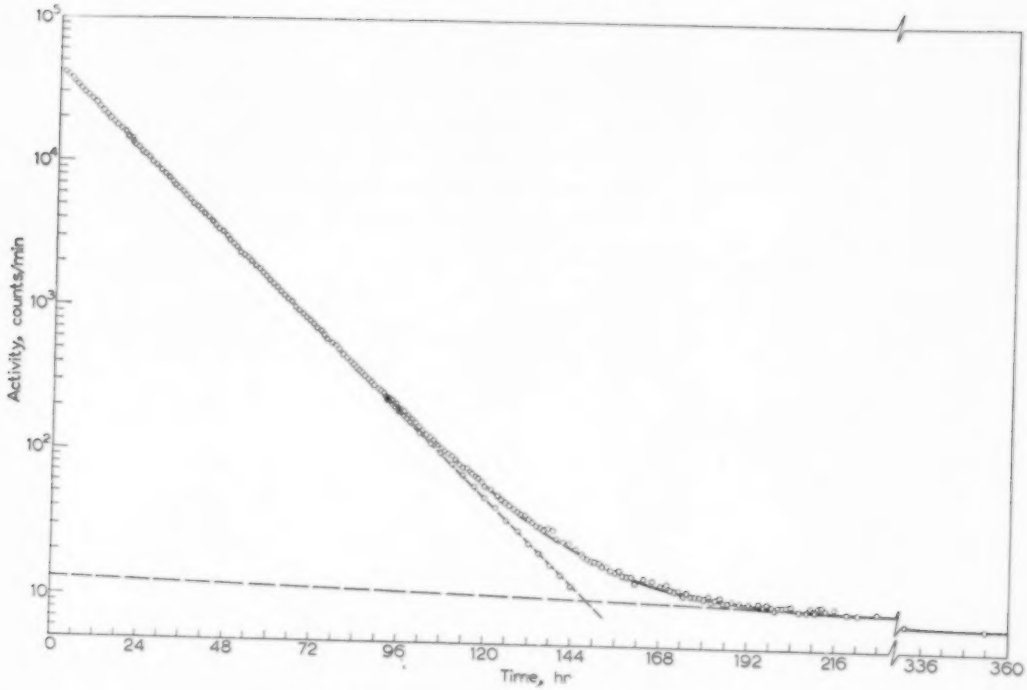

FIG. 2.—Composite decay curve for potassium-42.

TABLE 2.—COMPARISON OF RESULTS WITH PREVIOUS DATA

Branching fraction	Half-life (hr)	Reference
0·184 ± 0·014	12·37 ± 0·09	This work
	12·4 ± 0·2	(8)
0·30		(9)
0·16		(10)
0·25	12·44 ± 0·10	(11)
0·17 ± 0·01	12·5 ± 0·2	(12)
	12·5 ± 0·2	(13)
0·200 ± 0·01	12·44 ± 0·08	(14)
	12·516 ± 0·007	(15)
0·182		(16)
0·108 ± 0·006		(17)

(8) D. G. HURST and H. WALKE, *Phys. Rev.* **51**, 2033 (1937).
(9) E. BLEULER and W. ZUNTI, *Helv. Phys. Acta* **20**, 195 (1947).
(10) K. SIEGBAHN and A. JOHANSSON, *Arkiv. Mat. Astron. Fysik* **34A**, Paper No. 10, pp. 15–16(1947).
(11) K. SIEGBAHN, *Arkiv, Mat. Astron. Fysik* **34B**, Paper No. 4, pp. 1–7 (1947).
(12) W. S. LYON and B. KAHN, U.S.A.E.C. ORNL-1276 (1952).
(13) W. K. SINCLAIR and A. F. HOLLOWAY, *Nature, Lond.* **167**, 365 (1951).
(14) B. KAHN and W. S. LYON, *Phys. Rev.* **91**, 1212 (1953).
(15) P. R. J. BURCH, *Nature, Lond.* **172**, 361 (1953).
(16) L. KOERTS, A. SCHWARZSCHILD, R. GOLD and C. S. WU, *Phys. Rev.* **95**, 612A (1954). (Verbal report to *Nuclear Science Abstracts*, Tech Info Ext., Oak Ridge, Tenn.)
(17) E. W. EMERY and N. VEALL, *Proc. Phys. Soc.* A **68**, 346 (1955).

long-lived impurities represented only 0·03 per cent of the initial activity but became significant after approximately seven half-lives. The data was analysed by the method of least squares yielding a value for the half-life of 12·37 ± 0·09 hr.

Table 2 presents a comparison of the results obtained in this work with previous data for ^{42}K. The accuracy of the measurements of the branching fraction is given

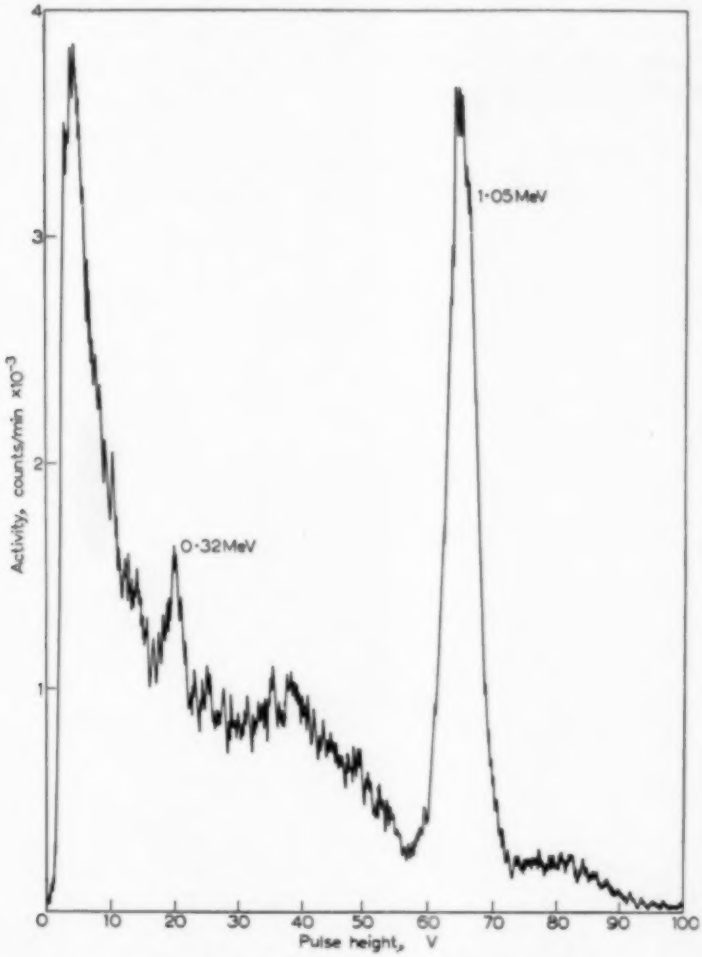

FIG. 3.—Pulse height spectrum of unpurified fraction.

as the probable error and was calculated from the probable error for each term in equation (3).

The accuracy of the branching fraction derived in this work has the advantage of depending primarily on the accurately determined value of E_γ, and to a much lesser extent on E_β although the latter is also determined accurately by the described methods. In addition the importance of measuring I_γ and N_β at early times in the absence of significant impurities (less than 0·1 per cent) was realized as shown by the decay curves and pulse height analysis.

During the course of measurements on Sample No. 10 described above a γ-pulse height measurement was made on the fraction of the activity not treated by ion exchange. The spectrum obtained (Fig. 3) showed energies at 1·05 MeV and a weak 0·32 MeV line. The former may be attributed to ^{86}Rb on the basis of γ-energy and half-life measurements. The latter corresponds in energy to the weak γ-ray reported by other workers to be present in the decay scheme of ^{42}K and whose relative abundance with respect to the 1·5 MeV γ-ray (as 100) has been given as 1·5,[18] 10,[19] and 0·8.[20] Insufficient activity precluded quatitative measurements of the half-life of this peak which appeared to decay with a half-life shorter than ^{86}Rb and longer than ^{42}K.

[18] N. H. LAZAR and P. R. BELL, *Phys. Rev.* **95,** 612A (1954). (Verbal report to *Nuclear Science Abstracts,* Tech. Info. Ext., Oak Ridge Tenn.)
[19] V. CAPPELLER and R. KLINGELHOFER, *Z. Naturf.* A **9,** 1052 (1954).
[20] A. V. POHM, R. C. WADDELL and E. N. JENSEN, *Phys. Rev.* **101,** 1315 (1956).

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THE INFRA-RED SPECTRUM AND STRUCTURE OF $K_4[Ni(CN)_3CO]_2$

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and
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Abstract—The infra-red spectrum of $K_4[Ni(CN)_3CO]_2$ has been determined, and possible structures for the anion are discussed.

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THE structures of the binuclear complexes $K_4[Ni^I(CN)_3]_2$[1,2] and $K_6[Co^{II}(CN)_5]_2$[2] have recently been studied by infra-red spectroscopy. While it was stated[1] that the former compound appears to have bridging CN groups, this conclusion has been shown to be incorrect[2] and the spectral data agree well with a structure consisting of two planar $Ni(CN)_3$ groups linked by a nickel–nickel bond; a metal–metal bond in the cobalt compound was also indicated. Further, the infra-red spectrum of the compound $K_2[Ni^0(CN)_3NO]$ has been examined and strongly supports a tetrahedral type of structure (symmetry C_{3v}) for the anion.[2] In this paper the infra-red spectrum and its interpretation in terms of anion structure are reported for $K_4[Ni^I(CN)_3CO]_2$. The formula given, with a binuclear anion is based upon the reported diamagnetism[3] since the $[Ni(CN)_3CO]^{-2}$ group would have an odd number of electrons.* Beyond this, however, a number of structures for the binuclear anion may be imagined and the infra-red spectrum together with some other considerations serves to limit the number of acceptable models. While such an analysis does not lead to an unambiguous assignment of structure it appears desirable to carry it through since the only known method of preparation and the properties of the material appear to preclude the possibility of obtaining the sort of crystals necessary for definitive X-ray work.

EXPERIMENTAL

The compound was prepared by the method of NAST and ROOS;[3] it is obtained as yellow hygroscopic crystals. (Found: K, 32·18; Ni, 24·0; C, 19·63. Calc. for $K_4[Ni(CN)_3CO]_2$: K, 32·76; Ni, 24·18; C, 19·45 per cent). The carbon analysis was made by measuring the carbon monoxide evolved on heating the compound with 50 per cent sulphuric acid.

The infra-red spectrum was taken in nujol mulls using a Perkin–Elmer Model 21 spectrophotometer with sodium chloride optics. The spectrum is shown in Fig. 1. The four strong bands are at frequencies of 2135, 2055, 1983 and 1905 cm^{-1}.

* *Note added in proof*: Measurements of ionic weights of nickel cyanide complexes by R. NAST and H. BÖHME, *Z. Naturf.* **13b**, 625 (1958) have recently confirmed that the carbonyl cyanide anion is indeed binuclear.

[1] M. EL-SAYED and R. K. SHELINE, *J. Amer. Chem. Soc.* **78**, 702 (1956).
[2] W. P. GRIFFITH and G. WILKINSON, *J. Inorg. Nucl. Chem.* **7**, 295 (1958).
[3] R. NAST and H. ROOS, *Z. Anorg. Chem.* **272**, 242 (1953).

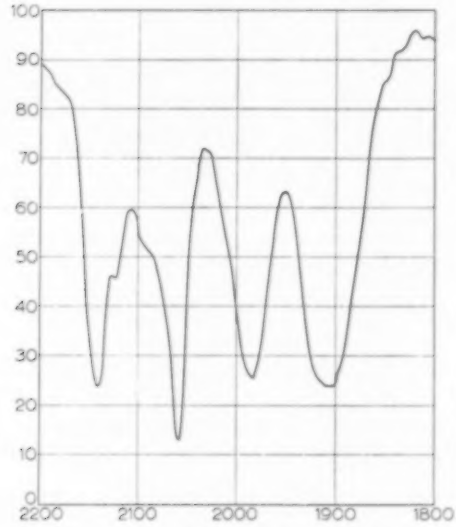

FIG. 1.—Infra-red spectrum of $K_4[Ni(CN)_3CO]_3$ in the CN and CO stretching region, taken in Nujol mull.

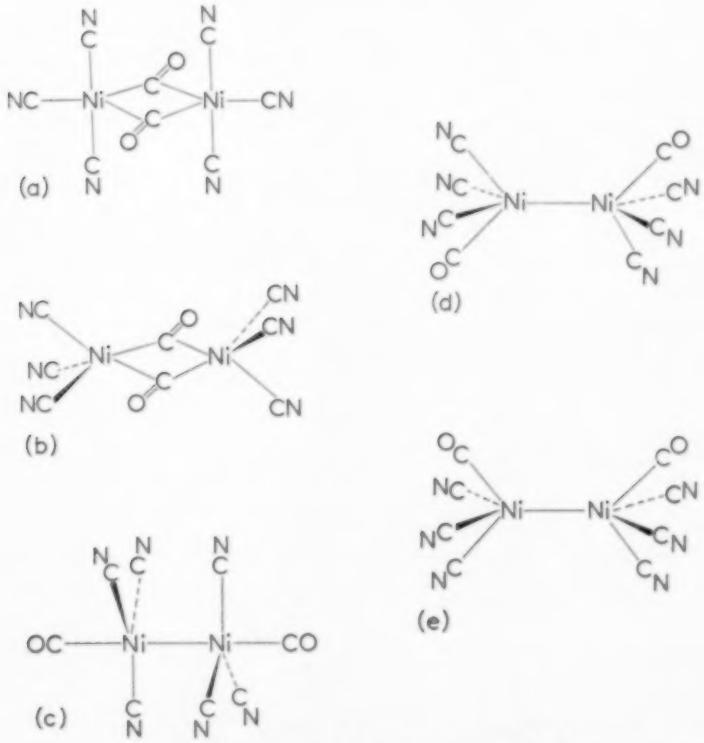

FIG. 2.—Structures considered for $[Ni(CN)_3CO]_3^{-4}$

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ANALYSIS

Possible structures* for the anion may first be broadly divided into those with bridging groups and those having only a direct nickel–nickel bond. For the former class, either CO or CN bridges might be considered. Since the proclivity of CO for forming ketonic bridges is well established while there is no known example of CN bridging in molecules of this type, only models with CO bridging will be considered. In this case the problem from the point of view of the symmetries and selection rules for various configurations is the same as in the case of $Co_2(CO)_8$ which has already been treated by several workers.[5,6] CABLE *et al.*[5] proposed that $Co_2(CO)_8$ has a structure, analogous to that shown for $[Ni(CN)_3(CO)]_2^{-4}$ in Fig. 2(a), obtained by joining two trigonal bipyramids at equatorial edges. In a note in proof they pointed out that a structure analogous to (b), obtained by joining two trigonal bipyramids *trans* fashion along slant edges also fits the observed spectrum. It has also been noted explicitly by CABLE and SHELINE[4] that these two structures cannot be distinguished on the basis of the infra-red spectrum. Later, FRIEDEL *et al.*[6] re-examined the spectrum of $Co_2(CO)_8$ reaching similar conclusions except that they suggested that the structure of type (b) is more likely on steric grounds. It does not seem to have been made clear in the papers cited on $Co_2(CO)_8$ that in both structures (a) and (b) it is not essential that the bond angles which would result from combination of trigonal bipyramids need persist in the dimers. It is only necessary that such changes as might occur do not alter the symmetry properties of the dimers. Thus, for example, in structure (a) the angles between the CN groups need not be 90°, but must only be equal; and in model (b) the angles between CN groups need not be 90°, 90° and 120°, but rather it is only necessary that the triangle defined by the three be isosceles. Furthermore, the structure constructed by CABLE *et al.* from two square pyramids (called by them IVB) has symmetry C_{2h} and thus is only a modification of structure (b) and of course has the same selection rules.

Models having Ni–Ni bonds are of two basic types, viz., structures of type (c) in

TABLE 1.—SELECTION RULES FOR CO AND CN STRETCHING MODES IN VARIOUS MODELS FOR $[Ni(CN)_2CO]_2^{-4}$

Model	Point group	Symmetry types of CO and CN stretches		Infra-red-active stretches	
		CN	CO	CN	CO
(a)	D_{2h}	$2A_{1g}$, B_{1u}, B_{2g}, $2B_{2u}$	A_{1g}, B_{2u}	3	1
(b)	C_{2h}	$2A_g$, A_u, B_g $2B_u$	A_g, A_u	3	1
(c)	D_{2d}	A_{1g}, A_{2u}, E_g, E_u	A_{1g}, A_{2u}	2	1
(c)	D_{3h}	A_1', A_2'', E', E''	A_1', A_2''	2	1
(d)	C_{2h}	$2A_g$, A_u, B_g, $2B_u$	A_g, B_u	3	1
(e)	C_{2v}	$2A_1$, A_2, B_1, $2B_2$	A_1, B_2	5	2

* CABLE and SHELINE[4] and NAST and ROOS[2] have previously expressed opinions as to the structure but have not presented any evidence.

[4] J. W. CABLE and R. K. SHELINE, *Chem. Rev.* **56**, 1 (1956).
[5] J. W. CABLE, R. S. NYHOLM and R. K. SHELINE, *J. Amer. Chem. Soc.* **76**, 3373 (1954).
[6] R. A. FRIEDEL, I. WENDER, S. L. SHUFLER and H. W. STERNBERG, *J. Amer. Chem. Soc.* **77**, 3951 (1955).

which there is a trigonal symmetry axis and structures (d) and (e) which can be regarded as built up from two $[Ni(CN)_3CO]$ moieties in which Ni uses bonds directed approximately to the apices of a square-based pyramid.

Two limiting cases of the structure type (c) are those with staggered (D_{3d}) and eclipsed (D_{3h}) configurations. Structure (d) has symmetry C_{2h} and structure (e) has symmetry C_{2v}. In Table 1 are shown the selection rules for CN and CO stretching vibrations in these cases. It should be noted that the symmetry of models of type (c) is quite independent of the value of the NC–Ni–CO angles so long as they are all equal, nor do the four carbon atoms—three of CN's and one of CO—at each end of structures (d) and (e) necessarily define a square; it is only required that the two C(CO) to C (adjacent CN) distances be equal and that the two C(CN) to C(CN) distances be equal.

DISCUSSION

We may first dispose of the very unlikely possibilities. These include structure (e) and any variants of (d) and (e) in which the relative rotational orientation of the two ends of the molecule is random as well as any models in which the end portions have no symmetry elements of their own. Also excluded are all models in which both CO groups are on the same nickel atom since the highest symmetry such a structure could have is C_{2v} and it is easily shown that this would have five infra-red-active CN stretches and two infra-red-active CO stretches. It must be noted that we are excluding the above structures on the ground that they require more than the observed number of infra-red bands. While such reasoning can often be dangerous due to the possibilities that

(a) some allowed bands may be present but very weak and

(b) accidental superpositions may occur;

it certainly seems unlikely that three or even four unobserved bands can be disposed of in this way.

The two variants of structure (c) considered both have one band too few. Crystalline field effects of three types could cause the appearance of more bands than are expected on the basis of the intrinsic molecular symmetry:

(1) If the molecules exist in the crystal at symmetrically distinguishable sites, it is possible that environmental effects—even if both site symmetries are as high as the molecular symmetry—could cause the frequencies of the molecules at one type of site to be different from those at another. It is not to be expected, however, that such effects could cause shifts of more than about 20 cm^{-1}. For example, shifts of 12–15 cm have recently been found in $(C_5H_5)_2Fe_2(CO)_4$ and attributed to this cause.[7] Since the minimum separation of any two bands in the spectrum of $[Ni(CN)_3CO]_2^{-4}$ is 72 cm^{-1} it is highly unlikely that this effect will permit one to rationalize model (c).

(2) It is possible that if the site symmetry in the crystal is lower than that of the molecule itself, crystal fields may cause a degenerate vibration to split. Again, however, such splitting would be expected to be much smaller than those found in the spectrum and this effect also cannot rationalize model (c).

(3) Finally, if the site symmetry is lower than the molecular symmetry, a vibration silent in the infra-red on the basis of the molecular symmetry could gain some intensity. What is very probably such an effect has been observed in the similar system

[7] F. A. COTTON, H. STAMMREICH and G. WILKINSON, *J. Inorg. Nucl. Chem.* In press.

$C_5H_5V(CO)_4$.[8] Since one of the two lowest bands, and almost certainly the lowest, must be due to the CO's one would then have either 1983 and 1905 cm^{-1} attributable to CO's or 2135, 2055 and 1983 cm^{-1} attributable to CN's, one in each case being spurious, due to a normally silent mode. In the latter case the spread of 152 cm^{-1} seems rather large for the frequencies due to a set of *equivalent* oscillators in view of experience with similar systems. The former spread in CO frequencies, 78 cm^{-1}, is also rather large under the circumstances. Thus structures of type (e) can be rationalized in only one way, (3), and then only using some dubious assumptions.

Selection rules for structure (d) of course agree perfectly with the observed spectrum without any reservations.* In terms of the number of absorption bands, structures (a), (b) and (d) are equally probable.

There now remains the question of whether the observed bands can be best assigned to a bridged or a non-bridged structure. Firstly it may be stated that in either case the bands at 2135 and 2055 may be assigned to CN stretching modes without question. The issue then may be decided on

(a) whether we can justify assigning the 1983 cm^{-1} band to a CN stretch since it is somewhat lower than the CN modes in numerous other cyanide complexes and

(b) whether we can justify assigning the 1905 cm^{-1} band to a bridging carbonyl.

The answer in each case would appear to be strongly favour a non-bridged model, and taken together to virtually eliminate a bridged structure. In view of the high negative charge on the anion it is quite possible that due to delocalization of this charge onto the ligands via $d\pi - p\pi$ bonding the CN bond order could be lowered below that found in other cases. As precedent for this the $Ni(CN)_4^{-4}$ ion has a CN stretching frequency as low as 1985 cm^{-1}[9] and in an analogous way it has recently been found[10] that the CO stretching frequencies in the series $[Ni(CO)_4$, $HCo(CO)_4$, $H_2Fe(CO)_4]$, $HFe(CO)_4^-$, $Fe(CO)_4^{-2}$ drop markedly in this order from ~2000 cm^{-1} to ~1750 cm^{-1}. The possibility of bridging CO groups absorbing as high as 1905 cm^{-1} is certainly remote on the basis of data for a number of other cases of CO bridging, where all reported frequencies are in the range 1770–1876 cm^{-1}. Moreover, delocalization of charge could also take place onto bridging CO groups and would tend to make the possibility of their stretching mode occurring as high as 1905 cm^{-1} extremely unlikely. It therefore appears that where the bridged structures are in agreement with the observed spectrum with regard to the number of bands, they would require some very unlikely assignments of these bands.

If absolute rigour be demanded it is not possible to eliminate any of the non-bridged structures, but in view of the above discussion the order of probability seems to be (e) $\ll$ (c) $\ll$ (d).

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* The two small shoulders apparent in Fig. 1 may be explained in various ways. While it is difficult to estimate their intensities relative to the stronger bands very accurately, they may be weak enough so that they may be attributed to CN vibrations in molecules containing ^{13}CN. One or both might also be attributed to small crystalline field effects of types (2) and (3) discussed previously.

[8] F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem.* **1**, 175 (1955).
[9] M. F. El-Sayed and R. K. Sheline, *J. Amer. Chem. Soc.* **80**, 2047 (1958).
[10] H. Stammreich. Private communication, to be published.

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J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 28 to 38. Pergamon Press Ltd. Printed in Northern Ireland

THE PREPARATION AND PROPERTIES OF A NEW PENTACYANOMANGANESENITRIC OXIDE ANION, $[Mn(CN)_5NO]^{2-}$, AND SOME OBSERVATIONS ON OTHER PENTACYANONITROSYL COMPLEXES

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Abstract—The yellow anion $[Mn(CN)_5NO]^{2-}$ may be prepared by oxidizing the purple $[Mn(CN)_5NO]^{3-}$ with ~6 N nitric acid in aqueous solution. Various salts may be isolated among which the silver, potassium and zinc salts have been prepared in pure form. The anion and its salts are only moderately stable. The silver and potassium salts are magnetically anomalous in the solid state; whereas the zinc salt in the solid state has a magnetic susceptibility corresponding to $\mu_{eff} = 1{\cdot}86$ BM. A magnetic susceptibility corresponding to $\mu_{eff} = 1{\cdot}76$ BM. was also obtained for the potassium salt in acetone solution. Infra-red and ultra-violet spectra of the ions $[Mn(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{3-}$ and several cyano anions isoelectronic with the latter are reported and discussed.

NITRIC oxide co-ordinates readily with metals forming a bewildering variety of compounds[1] which are for the most part of uncertain structure, especially in regard to the manner in which the NO group is bound. To date, however, only three pentacyanonitrosyl complex anions of metals of the first transition series have been reported, viz. salts of $[Mn(CN)_5NO]^{3-}$, $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5NO]^{3-}$. The nature of the last-mentioned is very uncertain[2] and it will not be further discussed here. The first two are isoelectronic and diamagnetic, and it has been proposed that they may be regarded as consisting of Mn^+, $5CN^-$, NO^+ and Fe^{2+}, $5CN^-$, NO^+ respectively.[3] The metal-NO bond is thus represented as a resonance hybrid of $M^- \leftarrow NO^+$ and $M \rightleftarrows N{=}O$.

In this paper we report the existence of a new, moderately stable complex ion, $[Mn(CN)_5NO]^{2-}$. The chemical, magnetic and spectral properties of this ion as well as of $[Mn(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ have been studied in some detail. The new ion is the first pentacyanonitrosyl anion with an odd number of electrons to be fully characterized.

EXPERIMENTAL

Preparation of $K_3[Mn(CN)_6]$. Two principal methods have been described for the preparation of this compound. One is a two-step synthesis involving first the preparation of $MnPO_4{\cdot}H_2O$ in relatively low yield (50–80 per cent) and then the conversion of this to the desired compound in good yield (90–95 per cent).[4] MEYER has also reported that it may be prepared directly by *in situ* oxidation of $K_4Mn(CN)_6$ with a current of air.[5] He reported yields of ~90 per cent. We have reinvestigated the MEYER procedure and find that with certain slight modifications yields of ~95 per cent can be

[1] For a partial listing see J. LEWIS, R. J. IRVING and G. WILKINSON, *J. Inorg. Nucl. Chem.* **7**, 32 (1958).
[2] N. V. SIDGWICK, *The Chemical Elements and Their Compounds*. Vol. 2. p. 1343 Oxford University Press (1950).
[3] D. P. MELLOR and D. P. CRAIG, *J. Proc. Roy. Soc. N.S.W.* **78**, 25 (1944).
[4] J. A. LOWER and W. C. FERNELIUS, *Inorganic Syntheses* Vol. 2, p. 213. McGraw-Hill, New York (1946).
[5] J. MEYER, *Z. anorg. Chem.* **81**, 390 (1913).

consistently obtained. Thus it appears more satisfactory than the two-step procedure. Good yields require attention to the following points:

(1) The $MnCO_3$ must be added to the KCN solution in small portions over at least 30 min. It should be finely powdered and any lumps which form in the reaction mixture should be crushed. This is necessary to provide maximum contact of the air stream with the $K_4Mn(CN)_6$ initially formed.

(2) A vessel about twice the size suggested by MEYER and the use of ~25 per cent more water facilitates the oxidation step. An oxidation period of ~24 hr was found adequate if the above suggestions are followed.

(3) Neither the reaction mixture nor solutions used in recrystallization should be heated above 80° because this causes decomposition to Mn(III) hydroxide. Rapid cooling during recrystallization tends to give a blue slimy deposit, difficult to filter. The product is actually pure enough for further synthetic use without recrystallization and was used directly for the preparation of $K_2[Mn(CN)_5NO]$.

The only aspect of the above procedure which might, in some circumstances, be undesirable is the 24 hr waiting period for air oxidation to occur. With a sacrifice in yield this may be avoided by oxidizing the $K_4Mn(CN)_6$ with $KMnO_4$, according to the reaction

$$MnO_4^- + 3Mn(CN)_6^{4-} + 2H_2O \rightarrow 3Mn(CN)_6^{3-} + 4OH^- + MnO_2.$$

An excess of an ice cold solution (2·5 g/100 ml) of $KMnO_4$ was added slowly, with vigorous stirring to the slurry of $K_4Mn(CN)_6$ also containing excess KCN cooled to 0°. After warming to room temperature the mixture was stirred for a further 15 min and filtered. The filter cake consisted chiefly of $K_3Mn(CN)_6$ but contained some MnO_2. The product was purified by recrystallization from 10 % KCN solution as in the MEYER method. The yield was ~75 per cent based on $MnCO_3$ used.

Preparation of $K_2[Mn(CN)_5NO]$. The literature contains three reports of preparations of this compound. It was first prepared in 1926 by MANCHOT and SCHMID[6] in very poor yield by passing nitric oxide into a solution containing manganous ion and potassium cyanide. BLANCHARD and MAGNUSSON[7] in 1941 reported a greatly improved yield when KOH was added to the reaction mixture. In 1948, HIEBER *et al.*[8] reported preparing the compound by treating $K_3Mn(CN)_6$ with a basic solution of hydroxylamine. Although the principles of this method are sound the directions given were vague and yields of no more than 70 per cent of somewhat impure material were at first obtained by us. The following procedure gives about an 85 per cent yield of very pure material.

Twenty grams of $K_3[Mn(CN)_6]$ are finely powdered and slowly stirred into 66 ml of a 10 per cent potassium cyanide solution so that the particles remain agitated and do not form a cake at the bottom. 87 g of a 10 per cent solution of hydroxylamine (made basic with KOH) is then added to the slurry and the mixture maintained at 75° for 15 min. The mixture is then filtered to remove $Mn(OH)_2$ and other solids. Glacial acetic acid is added to the filtrate until it is acid after which 830 ml of filtered, saturated solution of manganous acetate is added to precipitate $Mn_3[Mn(CN)_5NO]_2$. The manganous acetate should be added slowly with constant stirring in order to obtain an easily filterable precipitate which is filtered off after 30 min. The final yield may be increased from ~75 per cent to ~85 per cent if the filtrate from precipitation of $Mn_3(MnCN)_5NO]_2$ is slowly treated with one quarter of its volume of methanol, filtered after 10 min and the additional precipitate added to the first crop. The entire precipitate is washed with 100 ml of 50 per cent ethanol followed by 25 ml of 95 per cent ethanol and then ether and air dried.

The manganous salt, $Mn_3[Mn(CN)_5NO]_2$, is weighed and then mixed with sufficient 40% K_2CO_3 solution to give a 10 per cent excess of K_2CO_3 according to the equation

$$Mn_3[Mn(CN)_5NO]_2 + 3K_2CO_3 = 3MnCO_3 + 2K_2[Mn(CN)_5NO].$$

This paste is digested for 45 min with constant mixing and filtered with suction. The cake of $MnCO_3$ is washed with a volume of 50 per cent ethanol equal to one half the volume of the filtrate. The combined filtrate and washings are acidified with glacial acetic acid added slowly with stirring. The product is precipitated by adding 95 per cent ethanol, in about ten times the volume of the acidified filtrate, slowly over about 15 min. The precipitate and liquors are left to stand for 10–12 hr (on longer standing decomposition takes place), filtered and the precipitate washed with 95 per cent ethanol. The product is recrystallized by dissolving it in three times its weight of water; the solution is filtered

[6] W. MANCHOT and H. SCHMID, *Ber. Dtsch. Chem. Ges.* **59** *B*, 2360 (1926).
[7] A. A. BLANCHARD and F. S. MAGNUSSON, *J. Amer. Chem. Soc.* **63**, 2236 (1941).
[8] W. HIEBER, R. NAST, E. PROESCHEL and R. SCHUK, *Z. anorg. Chem.* **256**, 159 (1948).

and five times the volume of 95 per cent ethanol slowly added. This produces a crystalline precipitate which may be filtered after standing 2 hr and is then washed with 95 per cent ethanol and ether and air dried. This recrystallized product is markedly purer than that produced by the original HIEBER method in our hands. Yields were 80–90 per cent.

The dihydrate may be dehydrated by drying overnight in a vacuum with P_2O_5. For the hydrate, a weight loss on drying over P_2O_5 corresponding to 9·93% H_2O was found which is in agreement with the dihydrate formula reported by HIEBER (theory, 9·78 per cent). The anhydrous material gave the following analysis. (Found: K, 35·16, 35·20; Mn, 16·59, 16·65; C, 18·45, 16·80; N, 25·47, 24·97; CN, 39·00, 39·06. Calc.: K, 35·30; Mn, 16·53; C, 18·07; N, 25·31; CN, 39·14%). The direct carbon analysis is unreliable due to poor combustion of the compound even in the presence of $K_2Cr_2O_7$.

Reactions of $[Mn(CN)_5NO]^{3-}$. The hydrated and unhydrated solids are stable for at least three months in darkness or diffuse light, but after one week in air and strong sunlight there is considerable surface decomposition.

Solutions of the potassium salt, in the presence of air are attacked after a few minutes by ammonia and caustic alkalis. A precipitate of MnO_2 appears and increases steadily but even after two months the reaction is not complete at room temperature. At 100° reaction is complete within a few minutes. In the absence of air 6 N alkali hydroxides are virtually without effect at 80° for three days. Concentrated KCN solution is without effect. Stannous chloride and stannites have no effect. The precipitation reactions with heavy metals are essentially as reported by BLANCHARD.[7]

Silver ions give an initially pink precipitate which quickly turns white. An infra-red spectrum of the precipitate showed two peaks at ~2175 and ~2060 cm^{-1} due to CN stretches but no absorption at all between 1500 and 2000 cm^{-1}. Probably the silver ions destroy the anion, precipitating mainly AgCN. Ferric ions give a green-black precipitate which has strong absorptions at ~2110 and 1800 cm^{-1} suggesting (see discussion of spectra of other salts of the anion) perhaps that $Fe[Mn(CN)_5NO]$ is precipitated.

The action of acids is complex. Previous statements[8] failing to distinguish between the action of different acids are misleading. The acids studied here were hydrochloric, sulphuric, phosphoric, perchloric, acetic and nitric. At room temperature all these acids, except nitric, at concentrations up to 6 N, produce a red solution in 5 min or less and in the case of perchloric, a precipitate of $KClO_4$. The addition of alkali instantly reverses this colour change. These red solutions give precipitates with many heavy metal ions which appear to be identical with the corresponding precipitates of the $[Mn(CN)_5NO]^{2-}$ ion. It is therefore, probable that the red colour is due to a protonated form of that ion. The red ion cannot be extracted into ether. After about ½ hr at 80° or 24 hr at room temperature the red colour lightens through various shades of orange becoming finally bright yellow. Addition of alkali to this solution causes complete decomposition to hydroxides of manganese. During a few more hours at 80° or another day at room temperature the yellow colour fades slowly, finally leaving a colourless solution of the manganous ion. The yellow species could not be isolated by precipitation with heavy metal ions because the continuously changing nature of the solution made it uncertain when the precipitates were no longer due to the $[Mn(CN)_5NO]^{3-}$ ion or the red ion. Also it was not extracted by ether. HCN is continuously evolved during these changes.

The action of nitric acid is unique. If 6 N nitric acid is boiled and cooled it produces the same reddening effect at room temperature, but the solution suddenly turns an intense yellow after a few minutes at room temperature or immediately on warming. If the concentration is 8 N, the yellow colour is produced at room temperature without the induction period. Also concentrated nitric acid which is quite yellow (i.e. containing nitrogen oxides) when diluted even to 4 N produces the yellow colour instantly at room temperature. As shown below, this yellow colour is due to the ion $[Mn(CN)_5NO]^{2-}$. The dependence of the ease of oxidation on the presence of lower-valent nitrogen compounds suggest that they act as intermediates in the oxidation.

Acids more concentrated than 6 N break down the complex producing cloudy solutions and precipitates and ultimately the manganous ion. Sulphuric acid is especially efficient and quite useful for decomposition prior to analysis.

Solutions of $[Mn(CN)_5NO]^{3-}$ are decolorized by neutral hydrogen peroxide, turned red by basic peroxide and oxidized to $[Mn(CN)_5NO]^{2-}$ by acidic peroxide. All of these changes are reversed on addition of stannous or stannite ion or formic acid.

Preparation of $Ag_2[Mn(CN)_5NO]$. This compound was prepared by oxidation of $[Mn(CN)_5NO]^{3-}$

with nitric acid and precipitation of the salt by addition of Ag^+. Five grams of anhydrous $K_3[Mn(CN)_5NO]$ were dissolved in 15 ml of water at 0° and the solution filtered through a fine sintered glass disk. Twenty-five millilitres of yellow nitric acid (15·6 N) were diluted to 50 ml, cooled to 0° and added to the solution causing it to turn dark red. When allowed to warm to room temperature with stirring the solution turned yellow and oxides of nitrogen were evolved. The solution was then diluted to 120 ml, filtered if not clear, and 330 ml of 0·1 N $AgNO_3$ solution (10 per cent excess) added over a period of ~5 min with stirring. The precipitate was light brown to flesh-coloured and was allowed to stand with the supernatant liquid for 15 min. The supernatant liquid was then removed by suction filtration using a hardened filter paper. It was then washed successively with 10 ml each of water, ethanol and ether, all at 0°, and dried 2 hr with P_2O_5 in vacuum. It was ground in an agate mortar and redried in the same way for an additional 2 hr. Further drying causes no further weight loss. (Found: Ag, 49·72, 50·08; Mn, 12·76, 12·60; C, 14·54; N, 19·29; CN, 30·05, 30·15. Calc. for $Ag_3[Mn(CN)_5NO]$: Ag, 50·08; Mn, 12·75; C, 13·94; N, 19·51; CN, 30·19%).

Preparation of $Zn[Mn(CN)_5NO]\cdot XH_2O$. This salt was prepared in the same way as the silver salt up to the point at which the yellow solution containing nitric acid came to room temperature. The solution was then filtered if not clear but was *not* diluted since the zinc salt is moderately soluble. One and a half grams of $Zn(NO_3)_2$, as a saturated solution in water (5 per cent excess), were added producing a bright yellow precipitate which was then washed and dried as was the silver salt. The zinc salt was not anhydrous even when kept in vacuum for extended periods over P_2O_5. The water content varied somewhat. A typical preparation gave the following analysis. (Found: Zn, 20·36, 19·94; Mn, 16·33, 16·29; C, 17·78; N, 24·21; H, 1·96. Calc. for $Zn[Mn(CN)_5NO]\cdot 3{\cdot}3\,H_2O$: Zn, 19·24; Mn, 16·16; C, 17·67; N, 24·73; H, 1·96%).

Preparation of $K_2[Mn(CN)_5NO]$. Five grammes of $K_2[Mn(CN)_5NO]$ were dissolved in 15 ml of water and the solution filtered through a fine sintered glass disk. Yellow conc. nitric acid (15·6 N) was added dropwise (or, alternatively, 1·2 g bromine in 50 ml of ether was added slowly with agitation) to accomplish oxidation. The solution was swirled gently for 5 min as it became bright yellow and N_2O_4 was evolved. The solution was then evaporated to dryness by pumping while heating it to ~70° in a water bath. After about 4 hr of pumping the residue appeared quite dry and was yellow brown in colour. It was then scraped from the flask, ground in an agate mortar and stored in vacuum over P_2O_5 for 24 hr.

Five hundred millilitres of analytical reagent grade acetone, dried with magnesium sulphate then potassium carbonate, were siphoned into a thoroughly dry distillation apparatus. The first 100 ml of distillate were rejected and the next 200 ml were distilled directly into a dry 300 ml flask containing the crude, dry product and fitted with a drying tube to exclude water vapour. The mixture of acetone and powder was then shaken for 1 hr, the supernatant liquid siphoned off through a glass wool plug into a 500 ml suction flask and reduced to ~60 ml by vacuum evaporation. The solution at this point was usually clear yellow but when cloudy was filtered by suction as rapidly as possible through a hard paper. One hundred millilitres of sodium-dried ether were then added slowly to the acetone solution through a siphon. A brilliant canary-yellow, flocculent precipitate then formed and after 5 min it was filtered off by suction through a hardened paper as rapidly as possible, immediately washed on the paper with a mixture of 15 ml of dry acetone and 25 ml of dry ether and quickly placed in a vacuum desiccator with P_2O_5. This final filtration and washing must be done rapidly because atmospheric water vapour turns the edges of the filter cake brown within about 5 min. It was found that a small additional quantity of product could be isolated from the final yellow filtrates by evaporating to ~10 ml and adding ether, but the amount so obtained was hardly worth the effort. Yields averaged 40 per cent using either nitric acid or bromine as oxidant. (Found: K, 26·58, 26·55; Mn, 18·78, 18·85; C, 19·92; N, 29·84; CN, 44·50, 44·55. Calc. for $K_2[Mn(CN)_5NO]$: K, 26·67; Mn, 18·74; C, 20·48; N, 28·67; CN, 44·36%).

Chemical Properties of $[Mn(CN)_5NO]^{2-}$ *and its salts.* The ion in aqueous solution gives precipitates with the following other cations: mercurous (flesh coloured), cupric (light green), ferrous (dark green), nickelous (light yellow), cobaltous (red). The constitution of these precipitates has not been investigated.

The potassium salt is very soluble in water and quite soluble in ethanol. These solutions become cloudy within a few minutes. It is sparingly soluble in anhydrous acetone and the solutions are stable for periods from 0·5 to 2 hr. Solutions in dilute nitric acid remain clear for hours but this may only be due to solubility of the decomposition products.

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The silver salt seems to decompose spontaneously though slowly at room temperature evolving nitric oxide. It is slightly soluble in water but quickly decomposes to silver cyanide, manganous ions and other doubtful products.

The $[Mn(CN)_5NO]^{2-}$ ion can be reduced to $[Mn(CN)_5NO]^{3-}$ by stannous ions, stannites, formic acid, etc. Addition of alkali to the acidic solution causes it to turn red and this may be reversed by reacidification. The red alkaline solution is reduced with loss of colour by alkaline reducing agents and again turns red on addition of alkaline oxidizing agents. Evaporation of the red solution gave a complex mixture of solids apparently containing MnO_2 and $K_2[Mn(CN)_5NO]$.

Preparation of $K_3[Fe(CN)_5CO]\cdot 0{\cdot}6\ H_2O$. Two methods for the preparation of this compound are given in the literature.[9,10] The method of HIEBER *et al.*, calls for conversion of the nitroprusside ion to the pentacyano-aquo ion followed by treatment of an aqueous solution of this with carbon monoxide. We were unable to isolate any of the desired product by this method. The second method involves the reaction of a ferrocyanide solution with carbon monoxide under pressure and high temperature according to the equation:

$$K_4Fe(CN)_6 + 2H_2O + CO \rightarrow K_3[Fe(CN)_5CO] + HCOOK + NH_3$$

The published description of this method is rather vague; some of the details of our procedure are therefore given here.

Twenty-five millilitres of a saturated aqueous solution of $K_4Fe(CN)_6\cdot 3H_2O$ contained in a glass tube were placed in a steel pressure bomb. The bomb was charged with CO to 1000 lbs/in² and then heated to 300°C for 24 hr. After opening the bomb the solution was filtered and crude product precipitated by addition of ethanol. Purification was accomplished by recrystallizations which were carried out quickly in semi-darkness to minimize photochemical decomposition. The crude product was dissolved in ~10 ml of water, the solution made slightly acid with acetic acid and ethanol added to reprecipitate the product. This effectively frees it of potassium formate. It was then redissolved in water and dilute NaOH added to precipitate traces of iron as $Fe(OH)_3$. After filtration, the $K_3[Fe(CN)_5CO]$ was again precipitated by addition of ethanol, washed with ether and dried overnight in vacuum with P_2O_5. Analysis showed that under such mild drying conditions 0·61 mole of water of crystallization remained. (Found: Fe, 15·7; N, 20·78; H, 0·36. Calc. for $K_3[Fe(CN)_5CO]\cdot 0{\cdot}61H_2O$: Fe, 16·32; N, 20·46; H 0·36%). (Carbon analyses by combustion were ~4 per cent low, but this is a common occurrence with materials of this nature.) The yield was ~50 per cent and could probably be improved with care in the recrystallizations.

Magnetic susceptibilities. All measurements were made with a Gouy balance using split tubes which were calibrated with either water or Mohr's salt. Low temperatures were maintained using a glass Dewar vessel with liquid nitrogen and "Dry Ice"–acetone slush as coolants. Sample temperatures were measured by means of four copper-constantan thermocouples placed on the inner wall of the jacket along the length of the sample column (~6 in).

It was found that for $K_2[Mn(CN)_5NO]$ a sample which was analytically pure was not necessarily magnetically pure. The apparent susceptibility seems to vary with the length of time between the dissolution and final drying in the recrystallization process. For a typical sample the following apparent susceptibilities of the $[Mn(CN)_5NO]^{2-}$ ion were obtained where the length of time taken for recrystallization prior to measurement is increasing in the orper given: -61×10^{-6}, -49×10^{-6}, -36×10^{-6}. The value of -65×10^{-6} given in Table 1 was reproduced several times on samples recrystallized as quickly as possible.

As the compounds $Ag_2[Mn(CN)_5NO]$ and $K_2[Mn(CN)_5NO]$ are only moderately stable they were given special handling. The $Ag_2[Mn(CN)_5NO]$ was prepared and the susceptibility determined the same day. The $K_2[Mn(CN)_5NO]$ sample was recrystallized five times from acetone just prior to the susceptibility measurements and placed in a vacuum desiccator over P_2O_5. In order to pack the tube the desiccator, weighed Gouy tube, and other sundry apparatus were placed in a polyethylene bag suitably provided with rubber gloves, gas inlet and outlet and a Plexiglass window. The open end of the bag was folded over and clamped shut using wood strips and then thoroughly flushed with pre-purified nitrogen. To insure dryness a large glass tray containing P_2O_5 was also placed in the bag. The Gouy tube was then packed in the bag and closed with a ground joint. The tube was

[9] W. HIEBER, R. NAST and C. BARTENSTEIN, *Z. anorg. Chem.* **272,** 32 (1953).

[10] *Gmelins, Handbuch der Anorganischen Chemie*, Vol. 8, XIX, Part B, p. 740. Verlag Chemie, Berlin (1932).

weighed immediately on removal from the bag and then the joint was wax coated, after which the measurements were made.

A similar procedure was used in measuring $K_2[Mn(CN)_5NO]$ in acetone solution, the solution being prepared and the tube loaded and stoppered entirely in the dry nitrogen atmosphere. The measurements were made as quickly as possible and were completed before any detectable clouding of the solution. The entire time from initial addition of acetone to the solid to completion of the measurements averaged 15 min.

The zinc salt was packed quickly in air since it is relatively stable.

TABLE 1.—MAGNETIC SUSCEPTIBILITIES MEASURED IN THIS WORK

Compound	Temp. (°K)	Physical state	$\chi^g \times 10^6$	$\chi^{Mol.} \times 10^6$	$\chi^{Mol.} \times 10^6$ of anion[a]	$\chi^{Mol.} \times 10^6$ of metal ion[b]	μ(BM)
$K_4[Fe(CN)_6]\cdot 3H_2O$	301	Solid	−0·408	−172	−81	—	—
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	302	Solid	−0·377	−112	−76	—	—
$K_2[Fe(CN)_5CO]\cdot 0{\cdot}6H_2O$	298	Solid	−0·331	−113	−66	—	—
$K_2[Mn(CN)_5NO]$	301	Solid	−0·316	−104	−65	—	—
$Zn[Mn(CN)_5NO]\cdot 3{\cdot}3H_2O$	300	Solid	3·78	128_6	—	141_5	1·86[c]
	194	Solid	6·00	204_0	—	216_9	
	74	Solid	15·30	520_0	—	532_9	
$K_2[Mn(CN)_5NO]$	300	Acetone Sol'n	4·05	118_7	—	128_9	1·76[d]
$K_2[Mn(CN)_5NO]$	300	Solid	0·0109	3·20	—	105	0·50[e]
	196	Solid	0·0165	4·83	—	107	0·41[e]
	75	Solid	0·0421	$12{\cdot}3_4$	—	114	0·26[e]
$Ag_2[Mn(CN)_5NO]$	297	Solid	$0{\cdot}0065_7$	$2{\cdot}8_2$	—	127	0·55[e]
	193	Solid	0·0114	4·89	—	129	0·45[e]
	73	Solid	0·0279	$12{\cdot}0_4$	—	136	0·28[e]

[a] Obtained by correcting $\chi^{Mol.}$ for diamagnetism of alkali ions and water of hydration, using $\chi_{K^+}^{Mol.} = -13 \times 10^{-6}$, $\chi_{Na^+}^{Mol.} = -5 \times 10^{-6}$, $\chi_{H_2O}^{Mol.} = -13 \times 10^{-6}$.

[b] Obtained by correcting $\chi^{Mol.}$ for all diamagnetic contributions including that from Mn, using, in addition to the above, $\chi_{Zn^{++}}^{Mol.} = -10 \times 10^{-6}$, $\chi_{Ag^+}^{Mol.} = -24 \times 10^{-6}$, and $\chi^{Mol.}$ of an $[M(CN)_5NO]$ anion -76×10^{-6} as suggested by the diamagnetic salts listed in the table.

[c] Moment obtained from a Curie–Weiss law ($\mu = 2{\cdot}83\sqrt{[\chi_{Cor}^{Mol.}(T+\theta)]}$.) $\theta = -6{\cdot}3$°K.

[d] Calculated assuming Weiss constant, θ, equals zero.

[e] Each moment calculated as $\mu = 2{\cdot}83\sqrt{(\chi_{Cor}^{Mol.} T)}$.

Infra-red spectra. All spectra were recorded using a Perkin-Elmer Model 21 double beam spectrometer. Since the compounds studied were all insoluble in suitable organic solvents, all spectra were taken on Nujol mulls or pressed KBr disks. The great air-sensitivity of $K_2[Mn(CN)_5NO]$ necessitated special precautions in order to obtain an authentic spectrum. The Nujol mull was prepared in the nitrogen-flushed polyethylene bag (*vide supra*) and was placed in a desiccator before removal from the bag. It was then removed from the desiccator at the spectrometer and run immediately.

It was found that $Zn[Mn(CN)_5NO]\cdot XH_2O$ and, $Ag_2[Mn(CN)_5NO]$ gave very anomalous spectra when pressed in KBr disks. The spectrum of the silver salt was strongly affected even when just ground with KBr and the spectrum of the mixture run in Nujol. Similar but not quite so extreme results were obtained when the zinc salt was ground and pressed with KBr. The main effects are the appearance of a broad band at ~1800 cm^{-1}, a sharp band at ~1390 cm^{-1} and irregular changes in the CN stretching region. Grinding the silver salt with NaCl produces similar effects but not nearly so extensively. Nujol spectra of the zinc salt also consistently showed a band at ~1800 cm^{-1}. This band was always far weaker than the band at 1900 cm^{-1} (which we consider to be the authentic NO stretch) and its intensity relative to the 1900 cm^{-1} band varied noticeably. We believe that some reaction occurs between the zinc salt and the NaCl plates of the mull cell.

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The reactions of these salts with alkali halides seem certainly to involve reactions of the $[Mn(CN)_5NO]^{2-}$ anion itself. Similar reactions have been observed previously with other complexes.[11,12]

Ultra-violet and visible absorption spectra. These were measured on aqueous solutions of alkali salts of the various anions using a Cary Model 17 recording spectrophotometer. Extinction coefficients were calculated from the relation $\varepsilon = D/lc$, where ε is the molar extinction coefficient, l is the cell length, c is the molar concentration of the solution and D is the optical density, viz. $\log_{10}(I_o/I)$.

DISCUSSION

General

The general physical and chemical stability of salts of the new anion $[Mn(CN)_5NO]^{2-}$ are just about sufficient to make accurate physical studies of the usual kinds feasible. The isoelectronic iron complex $[Fe(CN)_5NO]^{-}$ is apparently very much less stable and its isolation has not yet been reported. It seemed reasonable to consider by extrapolation that perhaps the isoelectronic chromium anion, $[Cr(CN)_5NO]^{3-}$, might be quite stable. Before attempting to prepare it however, we learned that several of its salts have recently been isolated by WILKINSON and GRIFFITH[13] and they are considerably more stable than salts of $[Mn(CN)_5NO]^{2-}$.

In the isoelectronic sequence $[Fe(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{3-}$, $[Cr(CN)_5NO]^{4-}$, the first is extremely stable, the second moderately stable (much more so than $[Mn(CN)_5NO]^{2-}$ but the last has not yet been reported. Work directed toward its preparation has been undertaken.

Magnetic properties

Salts of $[Mn(CN)_5NO]^{-2}$. There are various *a priori* possibilities for the magnetic moment of the ion $[Mn(CN)_5NO]^{2-}$. It would certainly be reasonable to expect maximum spin-pairing, however, with ligands such as CN and NO. Thus if NO is considered to be co-ordinated as NO^+ the electronic configuration of the manganese ion would be T_{2g}^5, there would be one unpaired electron and the formal oxidation state of the manganese would be $+2$. If the NO were co-ordinated as the neutral molecule it would be possible to have only one unpaired electron in the complex (namely the one on the NO) only if the deviation from true octahedral symmetry were so great as to keep two of the three T_{2g} levels well below the remaining one. In this way the four electrons would be forced to pair up in these lower two orbitals Otherwise there would be altogether three unpaired electrons in the anion. Actually, it is found to have one unpaired electron. We think the formalism of NO^+ co-ordination is the better explanation since

(a) a large deviation from effectively octahedral symmetry does not seem likely, and,

(b) if we are to invoke the second argument in the case of $[Fe(CN)_5NO]^{-2}$ we would be led to expect two unpaired electrons, one on Fe and one on NO, whereas this ion is diamagnetic.

The statement that the ion $[Mn(CN)_5NO]^{-2}$ has one unpaired electron is based upon the magnetic moment of 1·76 BM measured on acetone solutions of the potassium salt and the moment of 1·86 BM measured on the zinc salt for which the Curie–Weiss law is followed with a very small Weiss Constant of $-6·3°K$. We have no

[11] L. H. JONES and M. M. CHAMBERLAIN, *J. Chem. Phys.* **25**, 365 (1956).
[12] V. W. MELOCHE and G. E. KALBUS, *J. Inorg. Nucl. Chem.* **6**, 104 (1958).
[13] G. WILKINSON. Private Communication. To be published shortly.

definite explanation to offer for the anomalous behaviour of the solid potassium and silver salts of this anion. It does not seem possible that there would be any antiferromagnetic interaction between ions of such large size and only one unpaired electron. In order for partial pairing of spins of electrons on different anions to occur by direct interaction it must be assumed that the electron is not localized on the metal atom. Of course the idea of NO^+ co-ordination is only a formalism and it may be that the electron does have appreciable density on the NO group so that in an appropriate lattice such electrons on neighbouring anions are partially paired.

The directions for preparation of $K_3[Mn(CN)_5NO]$, especially the long period of crystallization, are intended to produce a maximum yield of product. However, the material so obtained, while analytically pure contains traces of paramagnetic impurities (unidentified). It was found that when the recrystallization was carried out as rapidly as possible the most negative susceptibility values were obtained. In order to ascertain whether the best measurements give the true susceptibility of the $[Mn(CN)_5NO]^{3-}$ ion, salts of several closely related anions were carefully measured, viz. $K_4[Fe(CN)_6]\cdot 3H_2O$, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and $K_3[Fe(CN)_5CO]\cdot 0{\cdot}6H_2O$ which are all isoelectronic with $[Mn(CN)_5NO]^{3-}$. All of these compounds had been previously measured but it was difficult to know with what accuracy. (See footnotes to Table 1). While the value of -65×10^{-6} cgs units for $[Mn(CN)_5NO]^{3-}$ is still the lowest of the four, the variations ($-65, -66, -76, -81 \times 10^{-6}$ cgs units) are scarcely outside experimental error and moreover, while all the anions are isoelectronic small variations due to slightly differing mean radii of orbitals may well be expected. We therefore conclude that with care $K_3[Mn(CN)_5NO]$ can be obtained in a magnetically pure state and that it does not appear to be in any way magnetically anomalous.

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Infra-red spectra

Recently, LEWIS *et al.*[1] have published an extensive compilation of N—O stretching frequencies for a wide variety of complexes containing NO. They have concluded that in complexes where the NO group may be regarded, *formally*, as a co-ordinated NO^+ ion, the frequency falls in the general range 1650–2000 cm^{-1} as opposed to NO groups *formally* regarded as coordinated NO^- ions, which absorb much lower, in the range 1000–1200 cm^{-1}. These generalizations will be relevant in the following discussion.

$Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The spectrum of this compound has been reported before with respect to the N—O stretching frequency, LEWIS *et al.* cite 1925 cm^{-1} in KCl and 1938 cm^{-1} in KBr. We have examined the entire spectrum in the rock salt region rather carefully, including a partially deuterated specimen, since there are some uncommonly interesting features. The spectra in KBr disks and in Nujol were identical and the results are given in Table 2. The appearance of three CN stretching frequencies is exactly what would be expected for the ion $[Fe(CN)_5NO]^{2-}$ with C_{4v} symmetry. They are easily resolved. The position of the very strong NO stretching frequency at 1944 cm^{-1} is in satisfactory accord with previous observations but we believe our frequency value to be more accurate. The small splitting (see footnote (*b*) Table 2) may be due to the existence of environmentally distinguishable ions in the crystal; $\sim$12 cm^{-1} is a reasonable magnitude for such an effect.

The bands due to water of crystallization were studied in some detail because they were unusually sharp. Bands due to lattice water or co-ordinated water molecules

are more commonly very broad with little or no resolution of the symmetric and asymmetric stretches. In this compound the bands are extremely sharp (the 1615 cm^{-1} is 15–20 cm^{-1} wide at half height) and strong. Comparison of the spectrum of the partially deuterated compound with the spectra of H_2O, HDO and D_2O completely confirms the assignments indicated in Table 2. It will be noted that for the water of

TABLE 2.—THE INFRA-RED SPECTRA OF $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ AND PARTLY DEUTERATED ANALOGS

Compound	Absorption frequencies (cm^{-1})[a]				
	OH and OD str.		CN str.	NO str.	H_2O, D_2O HDO def.
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	3642	3563	2182, 2155, 2169	1944[b]	1615
$Na_2[Fe(CN)_5NO]\cdot 2(H,D)_2O$	3640	3562			1615
	2693	2630	2182, 2155, 2169	1944[b]	1182
	~3640	2654			1423
H_2O vapour[14]	3756	3652	—	—	1595
D_2O vapour[14]	2789	2666	—	—	1179
HDO vapour[14]	~3756	2719			1402

[a] Frequencies above 3000 cm^{-1} good to ± 10 cm^{-1}; those below 3000 cm^{-1} good to ± 3 cm^{-1}.
[b] This band may actually be double consisting of a very strong band at 1943 cm^{-1} and a strong shoulder at ~1955 cm^{-1}. Due to the breadth of the bands, this splitting is barely resolvable and cannot be said to be absolutely certain.

crystallization the stretching modes all occur ~100 cm^{-1} lower than for the gaseous molecules whereas the deformation frequencies are ~20 cm^{-1} higher. These shifts are in the same directions as, but very much smaller than, those observed in crystals where the water molecules are strongly hydrogen bonded. This evidence together with the sharpness of the bands suggests strongly that the water molecules in this substance form no strong hydrogen bonds. They may well be simply trapped in interstices in the lattice so that the main effect is to restrict their rotation and thus tend actually to sharpen the bands.

$K_3[Fe(CN)_5CO]\cdot 0{\cdot}6H_2O$. The infra-red spectrum of this compound, which was made primarily for use in the magnetic studies, has not previously been reported. The only absorption bands in the rock salt region (other than very weak and broad humps at 3300–3700 and 1570–1630 cm^{-1} due to water) are between 1900 and 2150 cm^{-1}. The CO stretching frequency is apparently stronger and broader than the CN stretching frequencies and the absorption in this region is not well resolved. It can be described as follows: 1990 (shoulder, medium), 2035 (shoulder, strong), 2052 (broad, strong), 2082 (strong), 2102 (sharp, strong).

$K_3[Mn(CN)_5NO]\cdot 2H_2O$. The NO stretching frequency is broad with a rather irregular shape suggestive of several shoulders separated by somewhat less than the least resolvable separation. The band has a rather sharp peak at 1725 ± 5 cm^{-1}, LEWIS *et al.* report 1730 cm.* Absorption in the CN stretching region consists of a

* For what they listed as the anhydrous compound but which we assume to have been the hydrate (see next section).

[14] See G. HERZBERG, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* pp. 280–282. Van Nostrand, New York (1945).

strong sharp peak at 2100 ± 10 cm with shoulders at ~2060 and 2138 ± 10 cm^{-1} The water of crystallization gives relatively broad peaks at 3240, 3370, a fairly sharp peak at 3580 with indications of other unresolved peaks in this region and a rather broad and bumpy peak at 1635 cm^{-1}. Evidently the water molecules are of several sorts and hydrogen bonded. Spectra in both Nujol and KBr disks were essentially identical.

$K_3[Mn(CN)_5NO]$. The spectrum of the anhydrous material has slight but characteristic differences from that of the dihydrate. The NO stretching band is quite broad and appears to consist of two closely overlapping peaks at ~1693 and ~1713 cm^{-1}. The absorptions in the CN stretching region consist of a strong sharp peak at ~2110 cm^{-1} with a weaker peak at ~2135 cm^{-1} and a weak shoulder at 2080 cm^{-1}. The indications that the water in the dihydrate is hydrogen bonded and the changes in the NO stretching absorption on its removal suggest that at least some of the hydrogen bonds are formed to the NO group.

$Zn_3[Mn(CN)_5NO]_2 \cdot xH_2O$. In this salt the characteristic frequencies of the $[Mn(CN)_5NO]^{3-}$ ion are considerably displaced to higher values. The NO stretching band is broad and strong, but relatively symmetrical and occurs at 1800 ± 10 cm^{-1} as compared to about 1700 cm^{-1} in the potassium salt. In the CN stretching region there is a very strong band at ~2145 cm^{-1} and a shoulder at ~2190 cm^{-1}. Thus these frequencies too are shifted up relative to those in the potassium salt. Spectra in Nujol and KBr are essentially identical. Water absorptions are very broad structureless humps centering around 3400 and 1625 cm^{-1}. While the frequency differences between this compound and the potassium salt are unusually large to be attributed to differences in lattice forces there appears to be no other explanation. It may be inferred that not too much significance should be placed on the exact positions of NO stretching bands in attempting to relate their frequencies to the electronic structures of the complex ions in which they occur.

$K_2[Mn(CN)_5NO]$. The spectrum of this compound was taken only in Nujol because of its air-sensitivity. The NO stretching band is very strong and peaks at 1885 ± 5 cm^{-1}. Relatively much weaker peaks were observed at ~2150 and 2100 cm^{-1}, the second of these being considerably weaker than the first. No other bands were observed in the rock salt region.

$Zn[Mn(CN)_5NO]$. As noted in the experimental section this compound reacts with alkali halides and only mull spectra are reliable. The NO stretching band is very strong and peaks at 1885 ± 10 cm^{-1}. Two CN stretching frequencies were observed, the stronger at 2195 cm^{-1} and the weaker at 2150 cm^{-1}.

$Ag_2[Mn(CN)_5NO]$. Like the zinc salt this compound interacts with alkali halides and only mull spectra can be considered reliable. The NO stretching band is very strong and is centered at 1880 ± 10 cm. Only one CN stretching band at ~2175 cm^{-1} was resolved.

Visible and ultra-violet spectra

It is a somewhat curious fact that of the isoelectronic anions $[Fe(CN)_6]^{4-}$, $[Fe(CN)_5CO]^{3-}$, $[Fe(CN)_5NO]^{2-}$ and $[Mn(CN)_5NO]^{3-}$ the first three are pale yellow, yellow-green and red, while the last one is a relatively intense red-purple. In order to see if these striking differences in colour might be due to any fundamental differences in the absorption spectra, the visible and ultra-violet spectra of all these anions

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were measured using aqueous solutions. The results are summarized in Table 3. Apparently the colour differences result from relatively small variations in band positions and intensities among spectra which are basically similar.

TABLE 3.—VISIBLE AND ULTRA-VIOLET ABSORPTION BANDS

Compound (in aqueous sol'n)	Band position		Molar extinction coefficient	Remarks
	(mμ)	(cm^{-1})		
$K_4[Fe(CN)_6]\cdot 3H_2O$	217	46,100	14,400	
	320	31,200	332	
	498	20,100	1·6	Existence questionable
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	—	—	—	Steeply rising absorption into vacuum UV
	390	35,600	24·6	
	~498	~20,100	~8·9	
$K_3[Fe(CN)_5CO]$	218	45,900	19,000	
	320	31,400	328	
	420	24,100	19·2	
$K_3[Mn(CN)_5NO]$	~220	~45,900	16,400	Very broad; possibly two close bands.
	348	28,600	114	
	540	18,500	23·6	

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ORGANOMETALLIC COMPLEXES—II[1]

ON THE EXISTENCE OF SOME MONONUCLEAR AND BINUCLEAR METAL-ORGANIC COMPLEXES

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Abstract—A theoretical discussion in terms of molecular orbitals is given of the relative stabilities of half-sandwich complexes of the transition metals of the type $C_nH_nMY_m$ and also of the symmetrical binuclear complexes $Y_mMC_nH_nMY_m$. The general conclusions are shown to be in agreement with the chemistry of known *cyclo*pentadienyl and benzene complexes and, in addition, to provide a reasonable theoretical basis for understanding known properties of a new range of metal-organic complexes.

DURING the last few years a number of complexes of transition metals with various unsaturated systems have been prepared in this laboratory[1] and it appears that the family of π-complexes may well be much larger than hitherto believed. In particular within this laboratory, there has been prepared a wide range of metal-organic complexes of the general formula $M_rY_s(C_nH_n)_t$ where M and Y denote the metal atom and attached ligand and r, s and t are integers. Many of these complexes are characterized by quite strong interaction between the unsaturated π-electron system and those orbitals of the central atom which have the required symmetry. Moreover, within the series C_4H_4, C_5H_5 and C_6H_6, the last two systems have been shown to form stable "sandwich" and "half-sandwich" compounds with a number of metals[2–6] and the possibility that the first compound may also form a half-sandwich π-complex has already been considered on theoretical grounds.[7] It is the purpose of this note to discuss from a theoretical viewpoint the relative stabilities of possible half-sandwich complexes of the general formula $C_nH_nMY_m$ and also of the symmetrical binuclear complexes $Y_mMC_nH_nMY_m$, where $4 \leqslant n \leqslant 8$, Y denotes an attached ligand and M a metal atom; the cyclic systems C_nH_n are referred to, perhaps a little loosely, as "aromatic".

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[1] Part 1: W. HÜBEL, E. H. BRAYE, A. CLAUSS, E. WEISS, U. KRÜERKE, D. A. BROWN, G. S. D. KING and C. HOOGZAND, *J. Inorg. Nucl. Chem.* **9**, 204 (1959).
[2] T. J. KEALY and P. L. PAUSON, *Nature, Lond.* **168**, 1039 (1951).
[3] G. WILKINSON, M. ROSENBLUM, M. C. WHITING and R. B. WOODWARD, *J. Amer. Chem. Soc.* **74**, 2125 (1952).
[4] E. O. FISCHER and W. HAFFNER, *Z. Naturf.* **10** B, 665 (1955).
[5] E. O. FISCHER and K. OFELE, *Ber. Dtsch. Chem. Ges.* **90**, 2532 (1957).
[6] B. NICHOLS and M. C. WHITING, *Proc. Chem. Soc.* 152 (1958).
[7] H. C. LONGUET-HIGGINS and L. E. ORGEL, *J. Chem. Soc.* 1969 (1956).

Mononuclear compounds

It is known[8] that the molecular orbitals of a cyclic π-electron system C_nH_n are determined by symmetry alone and may be written in the form:

$$\psi_j = \frac{1}{\sqrt{n}} \sum_{r=1}^{n} \exp\left(\frac{2\pi i j r}{n}\right) \chi_r$$

where

$$j = 0, \pm 1, \pm 2 \ldots + \frac{n}{2} \text{ for even } n$$

$$j = 0, \pm 1, \pm 2 \ldots \pm \frac{n-1}{2} \text{ for odd } n$$

and χ_r denotes the $2p_\pi$ atomic orbital of the r^{th} skeletal carbon atom. For purposes of comparison it is sufficient to classify these orbitals under the respective point

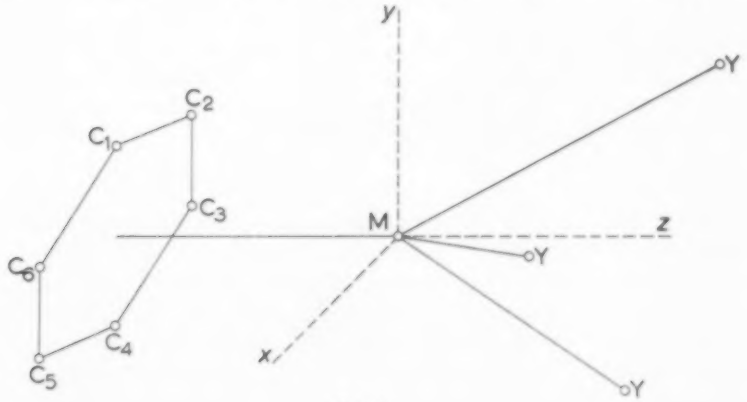

FIG. 1.

group D_n, that is, the extra symmetry elements due to the symmetry of the molecular plane are neglected, since these do not affect the subsequent arguments and are lost in the formation of the compound $Y_mM(C_nH_n)$. With this classification, these orbitals transform under their respective groups as given in column 2 of Table 1. The interaction of these π-orbitals with certain of the metal orbitals and also with those of a given ligand system will be considered.

The type of structure assumed is illustrated in Fig. 1 for the complex $C_6H_6MY_3$ and it is obvious that the only true symmetry element of the complete complex common to all cases is the bisecting plane, on the assumption that the molecule exists in either staggered or eclipsed configuration. Nevertheless, a classification can be retained for both π-orbitals and ligand orbitals in terms of their respective local symmetries as shown in Table 1 since this facilitates greatly the comparison between the different structures. The metal orbitals are classified with respect to the ring system: strictly speaking, the $3d_{(x^2-y^2)}/3d_{xy}$ orbitals should also be treated as belonging to the doubly degenerate representation for the case $n = 4$. However, in this particular case, interaction between the ring orbital (b_1) and the metal $3d_{xy}$

[8] E. HUCKEL, *Z. Physik* **70**, 204 (1931).

orbital is also possible so the classification is given as shown in Table 1. The last three columns denote the symmetry orbitals of groups Y_1, Y_2 and Y_3 respectively.

It is evident from the table that in all these complexes the molecular orbitals formed by the overlapping of the π-orbitals of the ring system and the metal orbitals will be of a closely related type. First, the stable, filled, totally symmetric orbital,

TABLE 1.—SYMMETRIES OF ORBITALS AND ENERGY LEVELS IN C_nH_n, AND COMPLEXES

n	C_nH_n orbitals			Metal orbitals	Ligand orbitals		
	Symmetry		Energy (β)		Y_1	Y_2	Y_3
4	(2)*	A_1	−2	s, p_z, d_{z^2}	A_1	A_1	A_1
		E_{1x}	0	p_x, d_{xz}		B_1	E_x
	(2)	E_{1y}	0	p_y, d_{yz}			E_y
		B_1	+2	d_{xy}			
		B_2		$d_{(x^2-y^2)}$			
5	(2)	A_1	−2	s, p_z, d_{z^2}	A_1	A_1	A_1
		E_{1x}	−0·618	p_x, d_{xz}		B_1	E_x
	(3)	E_{1y}	−0·618	p_y, d_{yz}			E_y
		E_2	+1·618	$d_{xy}, d_{(x^2-y^2)}$			
6	(2)	A_2	−2	s, p_z, d_{z^2}	A_1	A_1	A_1
		E_{1x}	−1	p_x, d_{xz}		B_1	E_x
	(4)	E_{1y}	−1	p_y, d_{yz}			E_y
		E_2	+1	$d_{xy}, d_{(x^2-y^2)}$			
		B_1	+2				
7	(2)	A_1	−2	s, p_z, d_{z^2}	A_1	A_1	A_1
		E_{1x}	−1·247	p_x, d_{xz}		B_1	E_x
	(4)	E_{1y}	−1·247	p_y, d_{yz}			E_y
	(1)	E_2	+0·445	$d_{xy}, d_{(x^2-y^2)}$			
		E_3	+1·802				
8	(2)	A_1	−2	s, p_z, d_{z^2}	A_1	A_1	A_1
		E_{1x}	−1·414	p_x, d_{xz}		B_1	E_x
	(4)	E_{1y}	−1·414	p_y, d_{yz}			E_y
	(2)	E_2	0	$d_{xy}, d_{(x^2-y^2)}$			
		E_3	+1·414	$d_{xy}, d_{(x^2-y^2)}$			
		B_1	+2				

* The figures in brackets denote the occupation numbers of a given orbital.

($j = 0$), will be stabilized by mixing with one component of the ($4s \pm 4p_z$) orbitals of the metal, one of which will be directed towards the ring system and the other towards the ligand group. Calculations of overlap suggest that, as in ferrocene,[9] the interaction of the $3d_{z^2}$ orbital is small and may be neglected. This type of stabilization, which is of μ-type with respect to the symmetry axis, will involve some charge transfer to the metal atom. Second, and most important, is the interaction of the doubly degenerate e_1 π-orbitals of the ring system ($p = \pm 1$), with the correctly orientated metal hybrids $3d_{xz}/4p_x$ and $3d_{yz}/4p_y$ and this will introduce a considerable

stabilization of such a complex. Lastly, the charge transfer to the metal atom involved in the totally symmetric class may be largely balanced by the overlapping of the empty e_2 π-orbitals of the ring system and metal $3d_{xy}$ orbitals; this interaction is of a δ-type with respect to the symmetry axis.

Similarly, the σ-orbitals of the metal-ligand bonding will arise by the mixing of the corresponding metal hybrid orbitals, orthogonal to those used above, with those ligand orbitals which have the correct symmetry. For example, the second component of $(4s \pm 4p_z)$ will overlap strongly with the totally symmetric ligand-group orbital, denoted by a_1 (Y). On this basis one may write the electronic structure of, for example, the complex $C_6H_6CrY_3$, as:

$$(a_1(\mathrm{Y})4s/4p)^2(e_x(\mathrm{Y})3d/4p)^2(e_y(\mathrm{Y})3d/4p)^2$$

$$(a_1 4s/4p)^2(3d_{z^2})^2(e_1 3d/4p)^4(e_2 3d)^4$$

where $(a_1 4s/4p)$ denotes the overall π-orbital formed by the interaction of the a_1 π-orbital of the aromatic system with the correct $4s/4p_z$ hybrid of the metal atom. The above structure denotes a normal eighteen electron complex. In this manner the electronic structures of a considerable number of complexes, both known and unknown, may be formalized and it is evident that to discuss their relative stabilities an assessment of the strength of bonding is required.

Detailed calculations for these systems do not seem, at the moment, the best method of estimating their relative stabilities, hence the following more qualitative arguments are employed. It seems very probable that in these complexes most of the bonding energy arises from the interaction of the e_1-orbitals, (more detailed calculations[9] suggest that in ferrocene it amounts to 75 per cent); consequently, the group-overlap integrals of the e_1 class are used as criteria for the relative stabilities of these systems and secondly, the relative positions of the e_1 π-orbitals of the ring system and the e_1 metal orbitals, that is the relative magnitude of their Coulomb terms. It will also be necessary to consider the variation of the atomic number of the central atom and also of the integers m and n.

The group-overlap integrals of the e_1 class involve the overlap between a metal orbital of the type $\frac{1}{\sqrt{2}}(\psi_{3d_{xz}} + \psi_{4p_x})$ and one component (e_x) of the doubly degenerate e_1 π-orbital of the ring system. It is necessary first to resolve the metal orbitals so that they are expressed in terms of orbitals defined with respect to the metal-carbon direction as z-axis (cp. reference (9)). By this means it is a simple matter to show that the group overlap integral $S(e_1, 3d/4p)$ takes the form:

$$\underline{S(e_1, 3d/4p)} = \frac{1}{\sqrt{2}}\left[\frac{\sqrt{3}}{2}\sin 2\omega \cos\omega S_{2p_\sigma 3d_\sigma} + \cos 2\omega \sin\omega S_{2p_\pi 3d_\pi} + (S_{2p_\sigma 4p_\sigma} + S_{2p_\pi 4p_\pi})\sin\omega\cos\omega\right]\sum_r C_r \cos\phi_r$$

where ω is the angle between the n-fold symmetry axis and the M—C bond and the summation is taken over the coefficients of the e_1 orbital; the summation is included to allow for the orientation of the metal orbitals with respect to the ring (cf. reference[9]).

[9] J. D. DUNITZ and L. E. ORGEL, *J. Chem. Phys.* **23**, 954 (1955).

The symbols $S_{2p_\sigma 3d_\sigma}$, $S_{2p_\pi 3d_\pi}$, $S_{2p_\sigma 4p_\sigma}$ and $S_{2p_\pi 4p_\pi}$ have the usual significance. In order to evaluate these latter integrals the internuclear distance was assumed to be 2·10 Å and the Slater exponents for the 3*d* and 4*p* orbitals assigned the values 1·6 ($\equiv\alpha_c$) and 0·90 respectively. This seems a reasonable choice of parameters for the following reasons. In the complexes so far investigated by X-ray analysis a metal-carbon distance of 2–2·10 Å has been observed;[10,11] moreover, for quite a number of transition metals α_{3d} as calculated from Slater's rules is close to α_c. The values of the integrals $S_{2p_\sigma 3d_\sigma}$ and $S_{2p_\pi 3d_\sigma}$ were taken from the tables of JAFFE.[12,13] The choice of 0·90 for α_{4p}, in good agreement with Slater's rules, is supported by some recent calculations on ferrocene[14] and also agrees with the assignment of YAMAZAKI.[15] It should also be noted that the integrals have been calculated involving the 4*p* functions using the rigorous Slater functions,[14] that is, a function calculated by the rigorous application of the Slater rules and, consequently, containing a fractional index. In fact this procedure is made necessary by the above choice of α_{4p} in as much as this value is sufficiently different from α_c to cause any interpolation between $S_{2p_\sigma 3p_\sigma}$ and $S_{2p_\sigma 5p_\sigma}$ to be invalid.

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TABLE 2.—GROUP OVERLAP INTEGRALS $S(e_1, 3d/4p)$

C_nH_n (n)	S
4	0·306
5	0·353
6	0·361
7	0·307
8	0·164

These integrals are listed above in Table 2; it is evident that in all cases the overlap is considerable and that the resultant bonding due to this symmetry group alone may well be sufficient to lead to the existence of stable complexes. However, an interesting trend is also observed, namely, that overlap appears to be a maximum for the five and six membered ring systems and to decrease markedly for the higher systems; this effect is, presumably, a purely geometric one due to the increase in the value of the angle ω with ring size. These results suggest therefore that complexes formed from the planar configurations of the higher membered ring systems are likely to be less stable than those of the lower members.

It is well known[16] that the bonding between any two orbitals is the stronger the more nearly equal are the Coulomb terms of the respective orbitals and on this basis one may discuss stabilities further. In the case of ferrocene it has been shown[17] that the $e_{1g}(e_1)$ level lies very close to the $e_1(3d_{xz,yz})$ level of the neutral iron atom;

[10] J. D. DUNITZ, L. E. ORGEL and A. RICH, *Acta Cryst.* **9**, 373 (1956).
[11] E. WEISS and E. O. FISCHER, *Z. Anorg. Chem.* **286**, 142 (1956).
[12] H. H. JAFFÉ and G. O. DOAK, *J. Chem. Phys.* **21**, 196 (1953).
[13] H. H. JAFFÉ, *J. Chem. Phys.* **21**, 259 (1953).
[14] D. A. BROWN, *J. Chem. Phys.* **29**, 1086 (1958).
[15] M. YAMAZAKI, *J. Chem. Phys.* **24**, 1260 (1956).
[16] C. A. COULSON, *Valence* p. 71. Clarendon Press, Oxford (1953).
[17] W. MOFFITT, *J. Amer. Chem. Soc.* **76**, 3386 (1954) and unpublished calculations.

that is, one may assume that the respective Coulomb terms of these orbitals are approximately equal. However, in the case of the complex $C_nH_nMY_m$, the interaction is being considered between $e_1\pi$-orbitals and metal $e_1(3d/4p)$ hybrid orbitals and for these latter the spectral data suggests that, in the case of iron, the absolute magnitude of the Coulomb term will probably be about 2 eV less than that of the pure $e_1(3d)$ orbital. One should then expect stronger binding, other things being equal, with an $e_1\pi$-orbital lying higher than that of the *cyclo*pentadienyl system; in fact such an orbital is provided by *cyclo*butadiene (a zero root). Since then, the overlap integrals are so similar in the two cases, one might expect that the *cyclo*butadiene complex is the more stable. Moreover, the e_1 orbital of the C_nH_n system lies at increasingly lower roots as n increases and so corroborates the argument based on Table 2 that the relative stabilities of these half-sandwich complexes will, for a given ligand Y, decrease up the series with increasing *n*. Of course, the above argument applies only to complexes containing iron as the central atom; however, as one proceeds along the first transition series the observed ionization potentials increase; a similar trend is also observed in the valence-state ionization potentials[18] and, consequently, it seems reasonable to suppose that the Coulomb term of the $3d/4p$ hybrid will also increase. The order of stability given above may, therefore, change as one proceeds along the series, and in particular, the *cyclo*pentadienyl complexes may become more stable. The variation of the nature of the ligand Y is undoubtedly important. It seems that the most essential property is the ability of the ligand to remove excess charge from the central atom by bonding of the d_n-p_n type. An accumulation of charge on the central atom would have an important effect on the Coulomb terms of the metal orbitals; indeed, it has been shown[14] that quite moderate charge transfer may change these terms by amounts comparable to the magnitude of the terms themselves. It follows then that the previous arguments might well be seriously affected by such charge transfer. If this argument is correct one would expect to find ligands such as carbonyl, cyanide and triarylphosphines present in these complexes.

The problem of the effect of the numerical values of *n* and *m* and of the type of central atom is more difficult to discuss. The decrease of m simply produces effectively non-bonding ($3d/4p$) orbitals and, as discussed previously,[7] the relative stabilities of complexes with different m values will depend on the $3d$-$4p$ separation, which is likely to be largest in positive ions. In connection with this point it is interesting to compare the sixteen and eighteen electron ions $[C_5H_5Fe(CO)_2]^+$ and $[C_5H_5Fe(CO)_2]^-$. The parent compound of the first ion is fairly definitely undissociated in most solvents[19] whereas the latter exists as a yellow anion in aqueous solution,[20] in other words, the sixteen electron structure exhibits a definite tendency to acquire a further electron pair if only by association. Further support for the stability of the eighteen electron complex is provided by the inability to obtain the paramagnetic $C_5H_5Fe(CO)_2$; in fact it is always the dimer which is produced in any possible reaction which might lead to this complex.

The electronic structures of the considerable range of half-sandwich cyclopentadienyl-metal complexes have already been fully discussed[21] and so no further comment is necessary.

[18] H. A. SKINNER and F. H. SUMMER, *J. Inorg. Nucl. Chem.* **4**, 245 (1957).
[19] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[20] E. O. FISCHER, *Angew. Chem.* **67**, 475 (1955).
[21] L. E. ORGEL, *J. Inorg. Nucl. Chem.* **2**, 315 (1956).

In fact in the case of $n = 7$ a *cyclo*heptatriene–molybdenum–tricarbonyl complex has been obtained in contrast[22] to a tropyllium complex which provides support for the above discussion. Recently a group of benzene derivatives of chromium tricarbonyl have been announced and quite definitely may be considered as half-sandwich π-complexes of the type discussed above.[6]

As indicated above, a wide range of new transition-metal complexes has been prepared during the last several years in this laboratory by HÜBEL *et al.*[1]. In particular, a very stable compound of the formula $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ has been

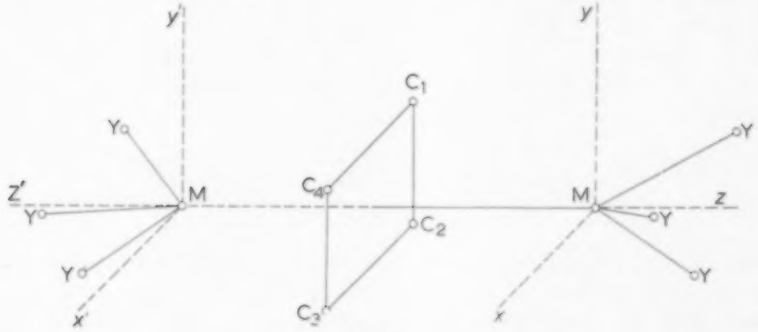

FIG. 2.

prepared; it has a melting point of 234°C and may be sublimed in high vacuum above 180°C. This compound may be formulated as a complex of the hitherto unknown tetraphenyl*cyclo*butadiene. A possible benzene complex is exemplified by the complex $Fe_2(C_6H_5C_2H)_3(CO)_6$ which on thermal decomposition gives 1,3,5-triphenylbenzene.

Binuclear complexes

In the subsequent sections the same type of qualitative arguments will be applied to a discussion of the relative stabilities of the binuclear complexes of the general formula $Y_mMC_nH_nMY_m$.

Again it is assumed that the molecular axis is the z-axis and, despite the fact that the only true symmetry element is still the bisecting plane, the orbitals of the constituent sustems will be classified by their local symmetries.

The type of structure assumed is illustrated in Fig. 2 for the complex $Y_3MC_4H_4MY_3$. If one distinguishes ligand and metal orbitals on opposite sides of the molecule plane of the cyclic system by single and double primes respectively, then the classification of the orbitals is identical with that given previously; however, for convenience it is given in Table 3.

It can be seen that the symmetry interactions of the metal, ligand and aromatic π-orbitals are almost identical with these in the mononuclear case, the only difference being that a given π-orbital now overlaps on either side of its nodal plane with identical metal $3d/4p$ hybrids. In other words the π-metal bonding in such complexes will consist of three-centre π-orbitals[23] embracing the two metal atoms and the

[22] E. W. ABEL, M. A. BENNETT and G. WILKINSON, *Proc. Chem. Soc.* 152 (1958).
[23] W. H. EBERHARDT, B. CRAWFORD, JR. and W. N. LIPSCOMB, *J. Chem. Phys.* **22**, 989 (1954).

π-system but will be split into exactly the same symmetry types as that of the mononuclear systems discussed previously. In the case of the interaction of a central π-orbital with two identical (and assumed non-interacting) d/p hybrid metal orbitals, it is shown in the appendix that the resultant orbitals (three-centre) will comprise firstly a non-bonding orbital the energy of which is identical with the Coulomb term

TABLE 3.—SYMMETRY CLASSIFICATION OF ORBITALS IN $C_4H_4(MY_2)_2$

Ligands	Metal	Aromatic	Metal	Ligands
a'_1	s', p'_z, d'_{z^2}	A_1	s'', p''_z, d''_{z^2}	a''_1
e'_y	$(p'_y d'_{yz})$	E_{1y}	$(p''_y d''_{yz})$	e''_y
e'_x	$(p'_x d'_{xz})$	E_{1x}	$(p''_x d''_{xz})$	e''_x
	(d'_{xy})	E_2	(d''_{xy})	
	$(d'_{(x^2-y^2)})$		$(d''_{(x^2-y^2)})$	

of the constituent metal orbital, secondly two symmetrically placed orbitals, bonding and anti-bonding respectively, the separation of which will depend on the relative magnitude of the two Coulomb terms and the resonance integral β. Thus, for example, the stable, filled totally symmetric π-orbital overlaps the $4s/4p_z$ hybrid situated on both metal atoms to give three three-centre orbitals of the above type. The interaction of the e_1 and e_2 classes will be similar. If, then, one denotes by ($4s'/4p'$, a_1, $4s''/4p''$) the overall three-centre orbital formed by the overlap of the a_1 π-orbital and the respective metal hybrid orbitals, the orbital configuration of the general binuclear complex may be written as

$$(e_1'(\mathrm{Y}),\ 3d'/4p')\ (a_1'(\mathrm{Y}),\ 4s'/4p')$$

$$(e_1''(\mathrm{Y}),\ 3d''/4p'')\ (a_1''(\mathrm{Y}),\ 4s''/4p'')$$

$$(3d'_{z^2})\ (3d_{z^2})$$

$$(4s'/4p',\ a_1,\ 4s''/4p'')\ (4s'/4p',\ a_1,\ 4s''/4p'')_0$$

$$(3d'/4p',\ e_1,\ 3d''/4p'')\ (3d'/4p',\ e_1,\ 3d''/4p'')_0$$

$$(3d',\ e_2,\ 3d'')\ (3d',\ e_2,\ 3d'')_0$$

where the zero subscript denotes a non-bonding orbital. Also neglected are any possible "end-on" interactions between the respective $3d_{z^2}$ orbitals. If this is a correct representation of the bonding in such complexes it follows that, owing to the incomplete filling of the overall three-centre orbitals, the electron configuration about each iron atom may not necessarily satisfy the inert-gas requirement since the stability of the complete complex will be related to the number of electrons occupying available bonding and non-bonding orbitals. However, if all the above orbitals are occupied then it follows that eighteen electrons are associated with each metal atom so that the inert gas structure is attained; such a case is most likely to occur when the $3d$-$4p$ and $4s$-$4p$ separations are smallest since the non-bonding levels are relatively low lying.

Although the order of stabilities of the above three-centre orbitals is difficult to

predict one conclusion can be drawn with regard to the relative stabilities of corresponding mono- and binuclear complexes, assuming similar metal–carbon distances in both. In this case the overlap between a given π-orbital and metal hybrid orbital will be similar for both types of complex and so one may assume that the resonance integrals, β, are also similar, especially since the same orbitals are being considered in each case. Now it is known[23] that for three-centre orbitals compounded from three identical atomic orbitals the stabilization energy is $\beta\sqrt{2}$, where β is the resonance integral between nearest neighbours, that is, the three-centre bonding orbitals of the binuclear complex are stabilized by $\beta\sqrt{2}$ as against β for the mononuclear case. However, it follows that since these three-centre orbitals bind two metal atoms to the ring the stabilization per metal atom is $\beta/\sqrt{2}$ in the binuclear case; consequently, this complex will be less stable. Of course, in view of the different Coulomb terms of the metal hybrids and π-orbitals this argument is not quite correct but since for the e_1 orbitals, which are the most important, these terms are not very different the above argument should be qualitatively correct. Moreover, there is the additional fact that those extra electrons which must be accommodated in the non-bonding orbitals will contribute no further stabilization energy.

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Again within this laboratory, there have been prepared[1] a number of complexes which may be formulated as of the above type and involving *cyclo*butadiene and benzene systems.

Many of these compounds are well characterized crystalline compounds and are quite stable thermally. It is interesting to note that, for example, the binuclear complex $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ decomposes at a temperature about 40° lower than the melting point of the corresponding mononuclear one (see above), in agreement with the predicted order of stabilities. These binuclear complexes, if this formulation is correct, are electron deficient in that each iron atom does not acquire an inert-gas structure since there are insufficient electrons to fill the non-bonding orbitals; however, as discussed above, due to formation of three-centre orbitals such a situation is readily envisaged, the difference being solely due to the number of electrons in the non-bonding orbitals. In this connexion one interesting deduction can be made with regard to the magnetism of the unsubstituted *cyclo*butadiene and benzene complexes of iron. The order of levels, neglecting ligand metal bonding, will probably be:

$$(3d'_{z^2})^2\ (3d''_{z^2})^2$$
$$(4s'/4p',\ a_1,\ 4s''/4p'')^2$$
$$(3d'/4p',\ e_1,\ 3d''/4p'')^4$$
$$(3d',\ e_2,\ 3d'')^4$$
$$(3d',\ e_2,\ 3d'')_0^4$$
$$(4s'/4p',\ a_1,\ 4s''/4p'')_0$$
$$(3d'/4p',\ e_1,\ 3d''/4p'')_0$$

and it is the filling of the last few orbitals which must be considered. The numbers of electrons available for these orbitals are 2 and 4 from *cyclo*butadiene and benzene respectively and, since the positions of these orbitals are determined by the Coulomb terms of the constituent metal orbitals only, it would be expected that the complexes

would be diamagnetic and paramagnetic respectively. This prediction has not been tested as yet.

Note added in proof

The recent publication of HOCK and MILLS[24] has revealed a quite unexpected structure for the complex $Fe_2C_{10}O_8H_4$ which might otherwise have been construed as a binuclear complex containing the *cyclo*butadiene ring. However, this structure, which contains one iron atom which is both σ- and π-bonded to a butadiene system and the other purely π-bonded, may be shown (D. A. BROWN, unpublished results) to involve bent 3 centre π-orbitals which are formally equivalent to the π-orbitals in the symmetrical case.

Appendix

One may consider the interaction of the two metal orbitals and central π-orbital in a binuclear complex.

let H_M denote the Coulomb term of the metal orbital (hybrid);
let H_{Ar} denote the Coulomb term of the aromatic π-orbital

and let β be the resonance integral between these two types of orbitals: the interaction between the metal orbitals is neglected.

The secular equation for such a system takes the form, with neglect of overlap,

$$\begin{vmatrix} H_M - E & \beta & 0 \\ \beta & H_{Ar} - E & \beta \\ 0 & \beta & H_M - E \end{vmatrix} = 0$$

and it follow immediately that the roots of this equation are given by:

$$E = H_M$$

$$E = \frac{H_M + H_{Ar}}{2} \pm \frac{\sqrt{(H_1^2 + H_2^2 - 2H_1H_2 + 8\beta^2)}}{2}$$

and thus the bonding and antibonding orbitals are distributed symmetrically about the mean of the Coulomb terms.

Acknowledgements—I wish to thank Drs. W. HÜBEL, E. H. BRAYE, C. HOOGZAND and E. WEISS for helpful discussions. This work constitutes part of a project being supported in this laboratory by Union Carbide Corporation, New York, and the author takes this opportunity to acknowledge with thanks this support.

[24] A. A. HOCK and O. S. MILLS, *Proc. Chem. Soc.* 233 (1958).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 49 to 57. Pergamon Press Ltd. Printed in Northern Ireland

ORGANOMETALLIC COMPLEXES—III*

ON THE POSSIBLE EXISTENCE OF METAL-ORGANIC COMPLEXES CONTAINING HETERO-ATOMS

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Abstract—A theoretical discussion based on molecular-orbital theory is applied to possible complexes of transition metals with various five and six-membered ring systems containing hetero-atoms or groups. The bonding in certain *cyclo*pentadienone and *p*-benzoquinone iron-complexes is discussed in the light of the above theory. It is suggested that complexes of the heavier transition metals and normal heterocyclic systems will be unstable.

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IN this paper the possible existence of complexes of the type $C_4H_4XMY_n$ and the corresponding binuclear type $C_4H_4X(MY_n)_2$ is discussed where X may be a hetero-atom or the group $>C=Z$ in which Z is a hetero-atom or hetero-group containing a lone electron pair. The discussion was inspired by the discovery[1] within this Laboratory of a number of substituted *cyclo*pentadienone complexes of transition metals. In addition to the above complexes derived from the *cyclo*pentadiene system similar complexes formed from $C_4H_4X_2$ will also be discussed. The discussion will follow closely that of the preceding paper and it will be found most convenient to commence with those systems in which X denotes the group $>C=\overset{\cdot\cdot}{Z}$.

Mononuclear complexes

The mononuclear complex $C_4H_4CZMY_n$ will be considered first; this complex, for the case $n=3$, is shown in Fig. 1. The isolated "aromatic" molecule, in which we consider one of the CH groups of the *cyclo*pentadienyl radical replaced by the group CZ, belongs to the point group C_{2v} and the six π-orbitals then transform as $4A_1 + 2B_2$. However, in the complex it is evident that the only true symmetry element is the bisecting plane σ_{yz} assuming a staggered or eclipsed model, and in fact the orbitals of the constituent systems are classified with respect to this plane. In the case of the complexes discussed in the previous paper, owing to the greater symmetry of the cyclic hydrocarbons as isolated systems, a greater separation of the π-orbitals of the aromatic system occurs and hence permits of a more restricted interaction with the metal orbitals. This is no longer true for the present type of complex and the only symmetry element which allows of any separation of the different types of metal π-orbital of the aromatic system interaction is the σ_{yz} plane. Of course, the ligands are still assumed to possess a local trigonal symmetry. With regard to this difference

* Paper II: *J. Inorg. Nucl. Chem.* **10**, 39 (1959).

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[1] W. HÜBEL, E. BRAYE, A. CLAUSS, E. WEISS, U. KRÜERKE, D. A. BROWN, G. S. D. KING and C. HOOGZAND, *J. Inorg. Nucl. Chem.* **9**, 204 (1959).

in the type of π-orbitals it is important to note that symmetry conditions alone require the bonding antisymmetric orbital (1 b_2) to be identical in form with one component of the doubly degenerate (e_1) orbital of *cyclo*pentadiene; it is this orbital which is responsible for so much of the bonding energy in ferrocene.

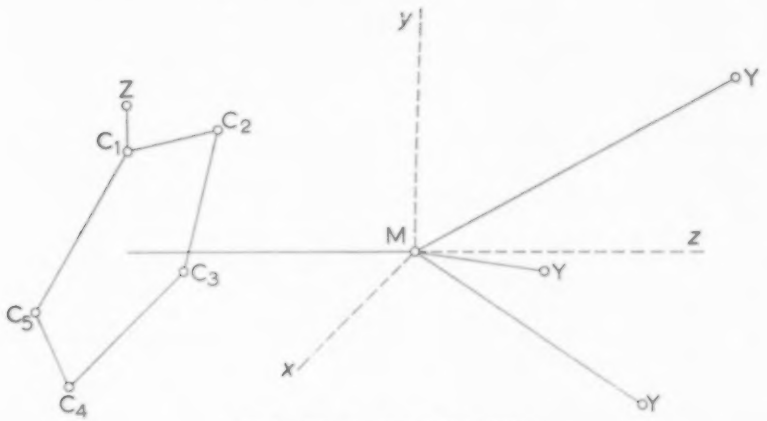


FIG. 1.—The complex $C_4H_4CZMY_3$.

In Table 1 the different orbitals of the respective systems are given and, for comparison, the orbital energies for the particular case of *cyclo*pentadienone[2] are included. The last column denotes the symmetries of the group orbitals of Y_3. The antisymmetric group is considered first. If p_x and d_{xz} are replaced by their sum and difference, it is obvious that one of these combinations will overlap with e_x(Y) and

TABLE 1.—SYMMETRY CLASSIFICATION OF $C_4H_4CZMY_3$

σ_{yz}	Aromatic	Orbital energy (β)	Metal	Ligands
		−2·95		
		−1·69	$s, p_z, d_{z^2}, d_{x^2-y^2}$	a_1(Y)
+	(4)* $4a_1$	−0·194	$(p_y d_{yz})$	e_y(Y)
		+1·85		
−	(2) $2b_2$	−0·618	$(p_x d_{xz})$	e_x(Y)
		+1·618	d_{xy}	

* Figures in brackets denote the occupation numbers of the orbitals.

the other quite strongly with the antisymmetric orbitals of the aromatic system; the overlap integral for the bonding antisymmetric orbital is identical with that given in Table 2, Paper II, for the case $n = 5$. The overlap of the $3d_{xy}$ is probably small so it will be neglected. The symmetric group is more complicated since there are now available four totally symmetric orbitals and six metal orbitals, all of which may

[2] R. D. BROWN, *J. Chem. Soc.* 2640 (1951).

interact. Again p_y and d_{yz} may be replaced by their sum and difference giving one orbital overlapping considerably with e_y(Y) and another orthogonal component which may overlap and so stabilize each of the totally symmetric π-orbitals of the "aromatic" system. Similarly, the 4*s* and 4p_z may be compounded to give one orbital overlapping strongly with a_1(Y) and the other directed towards the ring with a consequent further stabilization of the totally symmetric π-orbitals with the formation of a μ-type bond. The overlap of the 3d_{z^2} and 3$d_{x^2-y^2}$ is small and so it will be assumed, for simplicity, that these orbitals do not interact. The details of the mixing of the totally symmetric

TABLE 2.—POSITION OF LOWEST VACANT ORBITAL IN HETERO-SYSTEMS

h	k[a]	C_6H_6X (β)	C_5H_5CZ (β)	$C_6H_6(CZ)_2$(para)[a] (β)
1	1	+1·303	+0·187	−0·362
1	2	+1·618	0	−0·106
1	4	+1·618	+0·198	
1	9	+1·618	+0·390	
2	1	+1·115	−0·382	−0·918
2	2	+1·529	−0·217	(−0·322)
2	4	+1·618	0	−0·268
2	9	+1·618	+0·258	+0·172
3	1	+1	+0·431	−1·333
3	2	+1·346	+0·303	
3	4	+1·618	+0·130	−0·709
3	9	+1·618	−0·163	−0·179

orbitals are too difficult to discuss quantitatively but it seems evident that the π-orbitals will be stabilized by interaction primarily with the 4*s*/4*p* and 3*d*/4*p* hybrid orbitals.

If the above argument is correct it raises an interesting point. It is necessary for the metal 3d_{xz} and 3d_{yz} orbitals to be empty since they are overlapping with filled orbitals of both the ligand and aromatic system; consequently, in the case of the higher members of the first transition period, such as iron, the presence on the π-system of a suitable low-lying vacant orbital is required since this can then accommodate promoted electrons. In fact it is shown in Table 2 that such an orbital (3 a_1) is indeed available in the system C_5H_5CZ for a wide range of the parameters h and k. These parameters represent the variation of the Coulomb term (α_z) and the resonance integral β_{c-z} with the hetero-atom Z and are defined by the relations

$$\alpha_z = \alpha_c + h\beta_{c-c} \quad \text{and} \quad \beta_{c-z} = k\beta_{c-c}.$$

If, then, the totally symmetric π-orbitals of the ring system are labelled by $1a_1$, $2a_1 \ldots$, in terms of increasing energy and $\begin{pmatrix} na_1, & 4s/4p \\ & 3d/4p \end{pmatrix}$ denotes the stabilized orbital of the complex formed by the overlap of the na_1 π-orbital and the 4*s*/4*p* and

$3d/4p$ hybrids, the electronic structure of the complex $C_4H_4CZFeY_3$ may be represented as:

$$\left(a_1(\mathrm{Y}), \begin{matrix} 4s/4p \\ 3d/4p \end{matrix}\right)^2 \quad (e_x(\mathrm{Y}), 3d/4p)^2 \quad (e_y(\mathrm{Y}), 3d/4p)^2$$

$$(a_1, 3d_{x^2-y^2})^2 \quad (a_1, 3d_{z^2})^2 \quad (b_2, 3d_{xy})^2$$

$$(1b_2, 3d/4p)^2 \quad \left(1a_1, \begin{matrix} 4s/4p \\ 3d/4p \end{matrix}\right)^2 \quad \left(2a_1, \begin{matrix} 4s/4p \\ 3d/4p \end{matrix}\right)^2 \quad \left(3a_1, \begin{matrix} 4s/4p \\ 3d/4p \end{matrix}\right)^2.$$

It follows then that these complexes will be most stable when the $3d$-$4p$($4s$-$4p$) separation is smallest since all central orbitals involved in stabilizing the aromatic π-orbitals are hybrids: that is, the complexes should be most stable when they contain formally zero-valent central atoms. Of course, with the above electronic structure, this complex is formally an example of a twenty electron complex since all the six π-electrons occupy orbitals formed from orbitals of both the ring system and the central atom. On a simple valence–bond picture it is possible to regard these complexes as involving eighteen electrons if only the π-electrons of the C–C double bonds are considered to be involved. In fact such a description may not be necessarily in conflict with the molecular-orbital theory since only detailed calculations would show to what extent the metal orbitals are involved in some of the totally symmetric orbitals in the above scheme; it is possible that in certain cases the orbital may remain primarily on the aromatic system. It will be seen later, however, that in the complexes so far obtained of this type there is experimental evidence to show that the oxygen atom is involved in the metal-ring bonding. There is, of course, a good reason why in simple complexes of the first transition series those in which the metal atom is associated with eighteen electrons are the most stable ones. Any interaction of the metal and normal ligand orbitals will lead to the formation of stable bonding and unstable anti-bonding orbitals. Consequently, complexes containing more than eighteen electrons must contain electrons occupying anti-bonding orbitals or even free metal orbitals of the next quantum level; in either case the complex will be less stable than the corresponding eighteen electron case. However, this argument is no longer necessarily applicable when the ligand system possesses suitably low-lying vacant orbitals as in the above case. The function of the ligand Y will, presumably, be similar to that discussed in the previous paper.

Binuclear complexes

Complexes of the formula $Y_nM—C_4H_4CZ—MY_n$ may be expected to exist by an argument analogous to that given in Paper II and in fact this is found to be so but in this particular case, due to the number of orbitals involved, the discussion in terms of three-centre orbitals is not quite so simple.

The symmetry around each central atom of the complex is assumed to be the same as for the simple mononuclear half-sandwich complex considered above, that is having the bisecting plane as the only symmetry element. In this case, the symmetry classification of the orbitals is given in Table 3 below.

In the case of the b_2-class orbitals the interaction is similar to that given previously, thus the filled $1b_2$ orbital interacts with the $3d_{xz}/4p_x$ hybrids situated on each metal

centre to give three three-centre type orbitals, the position of the non-bonding orbital being determined by the Coulomb term of the above hybrid. Again, the interaction of the $3d_{xy}$ orbital is neglected. It is perhaps worth mentioning at this point that in the discussion of both the mono- and binuclear complexes any interaction between the upper ($2b_2$) orbital and the metal hybrids has been neglected since we feel that this

TABLE 3.—SYMMETRY CLASSIFICATION OF $C_4H_4CZ(MY_3)_2$

σ_{yz}	Ligand	Metal	Aromatic	Metal	Ligands
+	a_1'	s', p_z', d_{z^2}'	(4) $4a_1$	s'', p_z'', d_{z^2}''	a_1''
	e_y'	$d'_{(x^2-y^2)}$ $(p_y'd_{yz}')$		$d''_{(x^2-y^2)}$ $(p_y''d_{yz}'')$	e_y''
−	e_x'	$(p_x'd_{xz}')$ d_{xy}'	(2) $2b_2$	$(p_x''d_{xz}'')$ d_{xy}''	e_x''

orbital probably lies too high to be of any real value in stabilizing the filled metal orbitals, especially in view of the presence of the low-lying and empty $3a_1$ orbital. The interaction of the totally symmetric groups is more complicated since each π-orbital of the ring system can now overlap with two hybrids on each metal centre; consequently, it is no longer correct to speak of three-centre orbitals constructed from three orbitals only. However, it is shown in the appendix that such a system will lead to the formation of a stabilized (with respect to the free π-orbital) totally symmetric orbital, two "non-bonding" orbitals with energies equal to the Coulomb terms of the respective metal hybrids and finally two anti-bonding orbitals which lie above the corresponding non-bonding orbitals. In other words, it is meaningful to consider that each orthogonal A_1 π-orbital will be stabilized by this interaction and that the next available orbital will be effectively non-bonding; this will be denoted as before by a zero-subscript.

On this basis the electronic structure of the complex $Y_3Fe—C_4H_4CZ—FeY_3$ may be written as:

$$\left(a_1'(\mathrm{Y}), \begin{matrix}4s/4p\\3d/4p\end{matrix}\right)^2 \quad (e'(\mathrm{Y}), 3d/4p)^4 \quad \left(\begin{matrix}4s'/4p',\\3d'/4p',\end{matrix} \quad 1a_1, \quad \begin{matrix}4s''/4p''\\3d''/4p''\end{matrix}\right)^2$$

$$\left(a_1''(\mathrm{Y}), \begin{matrix}4s/4p\\3d/4p\end{matrix}\right)^2 \quad (e''(\mathrm{Y}), 3d/4p)^4 \quad \left(\begin{matrix}4s'/4p',\\3d'/4p',\end{matrix} \quad 2a_1, \quad \begin{matrix}4s''/4p''\\3d''/4p''\end{matrix}\right)^2$$

$$(3d'_{(x^2-y^2)})^2 \quad (3d''_{(x^2-y^2)})^2 \qquad \left(\begin{matrix}4s'/4p',\\3d'/4p',\end{matrix} \quad 3a_1, \quad \begin{matrix}4s''/4p''\\3d''/4p''\end{matrix}\right)^2$$

$$(3d_{z^2}')^2 \quad (3d_{z^2}'') \qquad (3d'/4p', \quad 1b_2, \quad 3d''/4p'')_0^2$$

$$(3d_{xy}')^2 \quad (3d_{xy}'')^2$$

$$(3d'/4p', \quad 1b_2, \quad 3d''/4p'')^2$$

where interaction between the other three orbitals is neglected. The order of filling

of the upper non-bonding orbitals is tentative and it would require a detailed quantitative investigation to determine the relative positions of these upper levels. It would appear from the above discussion that again the binuclear complexes are less stable than the mononuclear when, as in the case of iron for example, the upper non-bonding orbitals are filled.

Complexes of heterocyclic systems

In this short section possible complexes of the systems C_4H_4X in which the group X is a hetero-atom carrying a lone pair and no longer the group >C=Z are discussed. The five-membered heterocyclics might be expected to give stable complexes in view of the presence of the same antisymmetric orbital ($1b_2$) as that existing in the systems considered previously. On the assumption of a planar molecule the π-orbitals of the heterocyclic system will transform as $3A_1 + 2B_2$ and the types of interaction will be identical with those described above, save that there are now only three totally symmetric π-orbitals to be considered. This last fact is, however, crucial. The type of interaction occurring, namely, the stabilization of the filled ($1a_1$, $2a_1$ and $1b_2$) orbitals requires immediately the presence of a low-lying vacant orbital in which to place the extra metal electrons of the higher members of the first transition series. A normal molecular-orbital calculation was carried out for this molecule in which the parameters h and k (see above) were varied considerably. The results of column 3, Table 2 show immediately that for a reasonable range of these parameters such an orbital is not available. It would appear, therefore, that complexes of these systems will not be very stable.

Complexes of the system $C_4H_4(CZ)_2$

For this type of system it is possible to show that complexes analogous to those discussed above for the five-membered ring systems may be expected.

TABLE 4.—SYMMETRY CLASSIFICATION OF $C_4H_4(CZ)_2MY_3$

σ_{yz}	σ_{xz}	Aromatic	Metal	Ligands
+	+	$3B_{1u}$	$s, p_z, d_{z2}, d_{(x^2-y^2)}$	a_1(Y)
+	−	$3B_{2g}$	$p_y d_{yz}$	e_y(Y)
−	−	B_{3g}	$p_x d_{xz}$	e_x(Y)
−	−	A_{1u}	d_{xy}	

The isolated molecule, with the >CZ groups in para position, belongs to the D_{2h} point group and the π-orbitals then transform as $A_{1u} + 3B_{1u} + B_{3g} + 3B_{2g}$.[3] However, in the case of the complex $C_4H_4(CZ)_2MY_3$, for which a geometrical arrangement is assumed similar to that shown in Fig. 1 (Paper II), the local symmetry elements of the aromatic system are the planes σ_{yz} and σ_{xz}. It is the additional presence of the σ_{xz} plane which permits the aromatic-metal interaction to be more specific than in the case of the five-membered systems for which it is, of course, absent. The symmetry classification of the orbitals in this complex is given in Table 4.

[3] L. E. ORGEL, *Trans. Faraday Soc.* **52**, 1172 (1956).

The type of interaction is now obvious from the previous discussion and so will be given only briefly. On forming the usual orthogonal hybrids from the metal orbitals of a given symmetry class, it can be seen, first, that the filled $1b_{1u}$ and $2b_{1u}$ orbitals will be stabilized by overlap with one hybrid of $4s/4p_x$, and second, that the filled $1b_{2g}$ orbital will be stabilized by overlap with $3d_{xz}/4p_z$ orbital. The above interactions will involve charge transfer to the metal atom which is compensated, in part, by the transfer of electrons to the vacant low-lying $2b_{2g}$ orbital. Again any interaction of the $3d_{z^2}$ and $3d_{(x^2-y^2)}$ orbitals is neglected. The situation is, therefore, very similar to the previous case except that the four totally symmetric orbitals of C_4H_4CZ have been replaced by the $3b_{1u}$ and $3b_{2g}$ orbitals of the present system. Consequently, it follows that for the heavier transition metals it is again important that the π-system should possess a vacant and relatively low-lying orbital. It is evident from column 5, Table 3 that this condition is fulfilled for a range of hetero atoms Z[4]; in particular, it is true for *p*-benzoquinone ($h = 2$, $k^2 = 2$) and so complexes of this system may be expected to be stable. In addition, the occupation of such an orbital will also help to compensate for the charge transfer to the metal atom discussed above. It is difficult to compare the stabilities of such complexes with those formed from the corresponding five membered ring systems in view of the different bonding involved in the totally symmetric orbitals. However, if one considers simply the antisymmetric orbitals ($1b_{3g}$ and $1b_2$ respectively) then the five-membered ring complex may be expected to be more stable for the following reason. The stabilization of this group will depend both upon the overlap and on the relative values of the respective Coulomb terms. In Table 2 (Paper II) it is shown that the overlap integrals ($n = 5, 6$) are very similar so that it is the second factor which in this case is the more important. The b_{3g} orbital of $C_4H_4(CZ)_2$ lies lower than the $1b_2$ orbital of the corresponding C_4H_4CZ and so will possess a Coulomb term more different from that of the $3d/4p$ hybrid than the latter; it might then be expected that the five-membered systems should be the more stable ones.

To date no stable complexes with five-membered or six-membered heterocyclic compounds have been reported.* Mononuclear and binuclear derivatives of substituted *cyclo*pentadienone have been prepared in this laboratory.[1] These complexes are all well characterized crystalline compounds and possess considerable thermal stability. In addition to the normal carbonyl frequencies associated with carbonyl groups bonded directly to a metal atom there is also an intense band in the region 1610–1670 cm^{-1} which may be assigned to the ketonic carbonyl group of the substituted *cyclo*pentadienone ring. In addition to the *cyclo*pentadienone complexes similar half-sandwich compounds have also been obtained by direct synthesis from analogous ring systems in which the group Z is of the type >NR. The existence of these latter complexes supports the general nature of the arguments adduced above. It is interesting to note that the ketone carbonyl stretching frequency is observed in the tetraphenyl *cyclo*pentadienone complex at about 65 cm^{-1} lower than in the pure tetraphenyl*cyclo*pentadienone. This is in accord with the above orbital treatment

* *Note added in proof:* Since this paper was submitted for publication, the existence of a half-sandwich thiophene-chromium tricarbonyl complex has been reported (FISCHER and ÖFELE, *Z. Naturf.* **13 B**, 458 (1958). The existence of this compound is in accord with theory since the presence of a vacant low-lying orbital is no longer required in the case of chromium.

[1] V. GOLD, *Trans. Faraday Soc.* **46**, 109 (1950).

in as much as the interaction of the filled ($1a_1$ and $2a_1$) π-orbitals of *cyclo*pentadienone with the vacant metal hybrids will result in a lowering of the C=O bond order, especially since it is the $1a_1$ orbital which makes the largest contribution to this quantity. The binuclear complexes are also stable crystalline compounds and again exhibit a strong bond in the region 1610–1670 cm^{-1}.

Recently a tetramethyl benzoquinone complex has been obtained[5] which decomposes at about 50°C and is probably much less stable than the corresponding *cyclo*pentadienone complex. Again it is interesting to note that the infra-red spectrum contains a doublet at 1618 and 1639 cm^{-1} which shows a marked reduction over that observed in *p*-benzoquinone of 1667 cm^{-1}.[6] This evidence gives further support to the molecular-orbital description above.

Appendix

The interaction of the orbitals ψ_1 & ψ_2 is considered, with Coulomb terms H_1 & H_2, situated on centres *A* & *B*, with orbital ψ_3, Coulomb term H_3, situated on centre *C*. This situation is shown diagramatically below where β & γ represent the resonance integrals between ψ_1 & ψ_3 & ψ_2 & ψ_3, respectively.

The secular equation for such a problem, neglecting overlap, takes the form:

$$\begin{vmatrix} H_1-E & 0 & \beta & 0 & 0 \\ 0 & H_2-E & \gamma & 0 & 0 \\ \beta & \gamma & H_3-E & \gamma & \beta \\ 0 & 0 & \gamma & H_2-E & 0 \\ 0 & 0 & \beta & 0 & H_1-E \end{vmatrix} = 0$$

On expansion this takes the form

$$f(E) \equiv (H_1-E)(H_2-E)\{(H_1-E)(H_2-E)(H_3-E) - 2\gamma^2(H_1-E) - 2\beta^2(H_2-E)\} = 0$$

It is immediately evident that there are two effectively non-bonding orbitals at $E = H_1$, $E = H_2$. The other roots are found by solution of the equation.

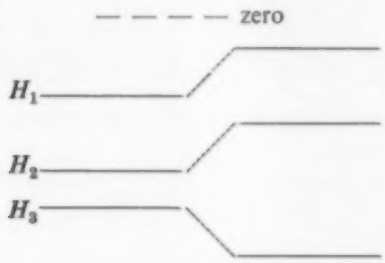
$$g(E) \equiv E^3 - E^2(H_1+H_2+H_3) + E(H_1H_2+H_2H_3+H_3H_1-2\gamma^2-2\beta^2) - (H_1H_2H_3 - 2\gamma^2H_1 - 2\beta^2H_2) = 0.$$

The roots may be written as $H_3+\delta_3$, $H_2+\delta_2$ & $H_1+\delta_1$ respectively; further let $|H_3| > |H_2| > |H_1|$. By consideration of the function $g(E)$ for decreasing E we obtain the regions in which the three roots will be situated:

$$\begin{aligned} E>0 \qquad g(E)>0 & \\ g(0) = -H_1H_2H_3 + 2H_1\gamma^2 + 2H_2\beta^2 & > 0 \\ g(H_1) = -2\beta^2(H_1-H_2) & < 0 \\ g(H_2) = -2\gamma^2(H_2-H_1) & > 0 \\ g(H_3) = -2\gamma^2(H_2-H_1) - 2\beta^2(H_3-H_2) & > 0 \\ g(-\infty) = -\infty & < 0 \end{aligned}$$

[5] H. W. STERNBERG, R. MARKBY and I. WENDER, *J. Amer. Chem. Soc.* **80**, 1009 (1958).
[6] M. L. JOSIEN, N. FUSON, J. M. LEBAS and T. M. GREGORY, *J. Chem. Phys.* **21**, 331 (1953).

It follows, therefore, that one root lies between zero and H_1, a second between H_1 and H_2 and a third below H_3 as shown in the diagram:



In other words the above type of interaction will lead to a stabilization of the lowest orbital and destabilization of the upper two orbitals.

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THE CHEMISTRY OF PROTACTINIUM—IV

SOME SPECTROPHOTOMETRIC OBSERVATIONS

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Abstract—True solutions of protactinium in hydrochloric acid, above 4 N in acid, are free from absorption bands down to at least 300 mμ. At lower wavelengths a band appears with its maximum below 210 mμ. The onset of hydrolysis and disappearance of the solvent extractability of the protactinium from the solution coincides with the appearance of an absorption band with its maximum at 260 mμ. Protactinium gives colour reactions with pyrogallol, cathechol, gallic and tannic acids as well as quinalizarin and 8-hydroxyquinoline. The absorption spectra of the first three complexes show maxima at 355, 323 and 343 mp. respectively; the molar extinction coefficients for the three complexes are $2{\cdot}6 \cdot 10^4$, $4{\cdot}8 \cdot 10^3$ and $5{\cdot}3 \cdot 10^3$. The pyrogallol complex seems suitable for the chlorination estimation of protactinium.

I. CHLORIDE SOLUTIONS

THREE spectrophotometric studies of solutions of protactinium in hydrochloric acid have already been reported. ELSON[1] refers to an investigation made by VAN WINKLE and JOHN which covered the absorption characteristics of solutions of varying acidity and chloride content. In dilute hydrochloric acid solution, between 0·5 and 2·0 M in acid, absorption bands were observed with maxima at 213 and 258 mμ. Increasing the acidity but maintaining a low chloride concentration moved these bands to longer wavelengths, the maxima appearing at 228 and 275 mμ, as well as introducing a third band with its maximum at 236 mμ. However, increasing the chloride concentration at 2 M acid moved the longer wavelength band back to 267 mμ. Finally, in 5–8 M hydrochloric acid maxima were found at 228, 247 and 269 mμ. The molar extinction coefficients were not measured but were estimated to lie in the range 10^3–10^4.

Very different results have been obtained by WELCH.[2] In freshly-prepared solutions above 5 M in acid an intense absorption band with its maximum at 208 mμ was observed. A much weaker diffuse band was also observed between 300 and 400 mμ. In such solutions the protactinium is present in a form extractable by a variety of organic solvents.[3] The extinction coefficient at the band maximum was very large and the band might well arise from electron transfer in the protactinium chloro-complex. In less acid solutions a further band appeared with a flatter maximum at 260 mμ. This band appeared to be associated with the hydrolysis of the protactinium species present in the more transparent solutions.

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[1] Q. VAN WINKLE, E. R. JOHN and R. E. ELSON, *National Nuclear Energy Series* Vol. 14A, p. 120. McGraw-Hill, New York (1954).
[2] G. A. WELCH, Thesis, London (1956).
[3] A. G. GOBLE and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* 7, 94 (1958).

FRIED and HINDMAN[4] have also published an absorption spectrum for a $4{\cdot}2 \times 10^{-5}$ M solution of protactinium in 1 M hydrochloric acid. Their curve shows a band with a very high extinction coefficient and a maximum below 220 mμ, with a shoulder extending from 240 to about 300 mμ. This shoulder might well arise from a band with its absorption maximum around 260–270 mμ.

Experimental

The long-lived α-active ^{231}Pa was used. The separation and preliminary purification of this material have been described in a recent publication.[5] The product from this process was subjected to the following additional purification.

First, the product was taken through three additional solvent extraction cycles. The solvent phase was washed twice on each occasion with 8 M hydrochloric acid and the protactinium subsequently re-extracted with 8 M hydrochloric acid which was 0·5 M in hydrofluoric acid. After the addition of two atoms of aluminium, added as anhydrous aluminium chloride, for each atom of fluorine in this solution a further extraction with di-*iso*propylketone was made. The final solvent extract was washed with 1·0 M hydrofluoric acid and the aqueous phase, containing all the protactinium, concentrated by evaporation in a platinum dish. In a 25 mg. purification the aqueous phases in the solvent extraction cycles amounted to 25 ml each. The final fluoride solution was concentrated by evaporation to 5 ml, cooled and the protactinium precipitated by the addition of barium chloride solution. The precipitated fluoprotactinate was separated and treated with concentrated sulphuric acid in the platinum basin. After evaporating to fuming for some hours the mixture was diluted to about 2 M in sulphuric acid and the supernatant solution separated. This solution was extracted with an equal volume of a solution of cupferron in amyl acetate.[6] The organic phase was separated and the protactinium recovered by washing it with 0·5 M hydrofluoric acid. This aqueous extract was treated with sulphuric acid and again evaporated to fuming in a platinum basin. The sulphuric acid solution was repeatedly evaporated almost to dryness to remove fluoride ions and finally the solution, which was now only faintly pink in the concentrated sulphuric acid, was diluted to about 2 per cent in sulphuric acid and twice the volume of 100 volume hydrogen peroxide added. After allowing 12 hr for precipitation, the peroxide was separated and washed with water. It was then dissolved in 8 M hydrochloric acid to give a solution containing 2 mg/ml of protactinium. Over a period of three weeks, however, about four-fifths of the protactinium separated in a precipitate. The fresh solution was used for the spectral observations except as otherwise specified.

The absorption spectrum of protactinium in chloride solutions was plotted for solutions of different compositions from 210–450 mμ using a Unicam spectrophotometer and calibrated 10 mm quartz cells. The hydrochloric acid used included both the commercial AnalaR product and a sample specially prepared from crystallized AnalaR sodium chloride and nitrogen-free sulphuric acid. The protactinium was added to the test cell in an 0·01 ml aliquot of the concentrated hydrochloric acid solution. Some of the solutions of lower acidity were re-examined after standing overnight. Just before these spectra were measured the extractability of the protactinium in the solution was determined by removing an aliquot of the solution, adjusting the acidity to 4·5 M in hydrochloric acid and equilibrating with an equal volume of di-*iso*propylcarbinol.

Results

The absorption spectra of solutions of protactinium in varying concentrations of hydrochloric acid, each containing 6 γ/ml of protactinium, were examined. The absorption spectra obtained are shown in Fig. 1. Measurements were also made on a series of solutions, comprising mixtures of lithium chloride and hydrochloric acid, containing the same concentration of protactinium and a fixed concentration, 10·2 M, of chloride ions, but varying acidities. These absorption spectra are shown in Fig. 2.

[4] S. FRIED and J. C. HINDMAN, *J. Amer. Chem. Soc.* **76**, 4863 (1954).
[5] A. G. GOBLE, J. GOLDEN, A. G. MADDOCK and D. J. TOMS, *Progress in Nuclear Energy—III, Process Chemistry* Vol. 2, p. 86. Pergamon Press, London, New York (1958).
[6] A. G. MADDOCK and G. L. MILES, *J. Chem. Soc.* Suppl. No. 2, S 248 (1949).

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FIG. 2.—Absorption spectra of solutions of protactinium of varying acidity but constant total chloride content. 1, 0·9 M; 2, 1·1 M; 3, 4·0 M; 4, 5·0 M; 5, 5·5 M; 6, 10·2 M. All solutions contain 6 γ/ml of ^{231}Pa and 10·2 M chloride.

FIG. 1.—Absorption spectra of solutions of protactinium in different concentrations of hydrochloric acid. 1, 1·0 M; 2, 5·0 M; 3, 7·0 M; 4, 8·5 M; 5, 9·5 M; 6, 10·2 M. All solutions contain 6 γ/ml of ^{231}Pa.

Attempts to reach the absorption maximum of the single band found in the more acidic solutions were unsuccessful because the absorption of the hydrochloric acid was too strong below 210 mμ. Specially prepared hydrochloric acid made from hydrogen chloride generated *in vacuo* from AnalaR sodium chloride and nitrogen-free sulphuric acid and doubly distilled water was not significantly more transparent than the ordinary acid. However, it is well known that aqueous spectrophotometric measurements are very difficult and often unreliable much below 220 mμ.

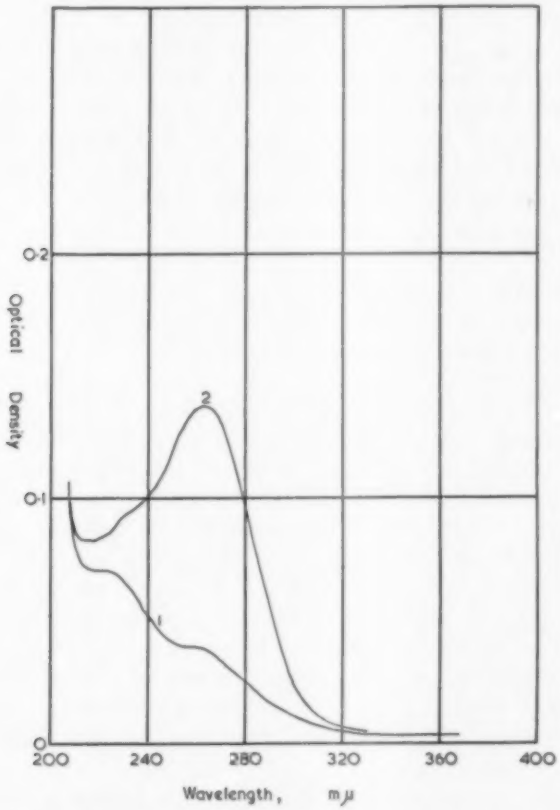


FIG. 3.—Absorption spectra of a solution of protactinium in 1·0 M hydrochloric acid before and after standing. Solution contains 6 γ/ml of protactinium. 1. Immediately after preparation. 2. 15 hr later.

Measurements made at higher concentrations of protactinium in solutions above 5 M in hydrochloric acid showed no evidence of any other absorption bands, except the hydrolysis band described below. When the solutions in 1 M and 2 M hydrochloric acid were re-examined after standing overnight a new band with a maximum at 260 mμ was found. The results for the 1 M acid are shown in Fig. 3. It will be observed that the optical density at the new maximum exceeds that at any wavelength in the spectrum of the fresh solution. The solvent extraction of the protactinium from the aged solutions was measured after diluting a 0·01 ml sample with 3 ml of 4·5 M hydrochloric

acid. In the case of the 15 hr old 1 M solution the extraction by an equal volume of di-*iso*propylcarbinol was found to have fallen to 2 per cent from a value of 78 per cent for the fresh solution.

Throughout these investigations[3,7,8] solutions of protactinium, even in strong hydrochloric acid, have eventually been found to "age" and suffer a radical change in the solvent extractability of the protactinium. In one closely observed case a solution in 6 M hydrochloric acid was stored for six weeks in a polythene vessel at 15–18° and maintained the same extraction properties during the whole of this period. However, at the end of this period during the course of one day the extraction under similar conditions fell from 99 per cent to 2 per cent. The resulting solution appeared to contain a colloidal protactinium compound. It was readily lost from solution by absorption on to surfaces and could gradually be separated in a high speed centrifuge. The colloidal properties of the solution continued to change with storage after the change in solvent extractability was complete. The reaction has all the characteristics of an hydrolysis followed by condensation and polymerization. The reaction was not reversed by increasing the concentration of hydrochloric acid to 11 M, or by heating.

It seemed desirable to determine whether this reaction in strongly acidic solution was essentially similar to the more rapid reaction in 1 M and 2 M acid solutions recorded above. A solution of protactinium in 4·5 M hydrochloric acid, containing 12 γ/ml of protactinium, was prepared and allowed to stand in a stoppered quartz absorption cell. The absorption spectrum and solvent extraction characteristics of the solution were measured at intervals of a few days. After nine weeks of storage the extraction coefficient suddenly began to fall, decreasing from 88 per cent to 3 per cent extraction under standard conditions in the course of three days. At the same time, a peak emerged in the absorption spectrum at 260 mμ where previously there was only a slight inflexion on the side of the lower wavelength band.

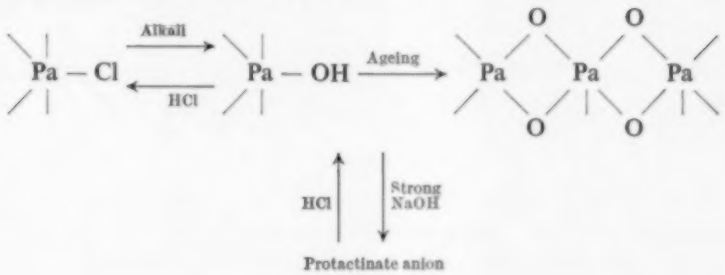
The same solution was now made 9 M in hydrochloric acid but the extraction did not return to its original value nor did the 260 mμ band disappear. However, after treating with 0·5 M hydrofluoric acid and then evaporating repeatedly with hydrochloric acid in a platinum basin, on diluting to 4·5 M in acid the solution was found to have regained its original extraction characteristics and to have lost the 260 mμ absorption band. More concentrated solutions of protactinium, even in 9 M hydrochloric acid, generally show some signs of the 260 mμ band.

It is concluded that the principal feature of the absorption spectrum of true solutions of protactinium in hydrochloric acid is a single band with a high extinction coefficient and a maximum below 210 mμ. It is probably an electron transfer band. Hydrolysis of the protactinium chloro-complex contained in these solutions gives a species, probably of high molecular weight and present in colloidal suspension, which gives a strong absorption band with a maximum at 260 mμ. At the same time the lower wavelength band develops a shoulder suggesting another band with its maximum about 225 mμ. The appearance of these bands coincides with the disappearance of the extractability of the protactinium. It seems possible that the absorption between 300 and 400 mμ reported by Welch might have been due to a trace of iron.

This behaviour of protactinium is qualitatively similar to niobium and may be

[7] J. Golden and A. G. Maddock, *J. Inorg. Nucl. Chem.* **2**, 46 (1956).
[8] A. G. Goble, A. G. Golden and A. G. Maddock, *Canad. J. Chem.* **34**, 284 (1956).

interpreted in terms of the following reactions:



Protactinium hydroxide may be precipitated from solutions of the chloro-complex by the addition of alkali. In very alkaline solutions some re-solution to produce a protactinate anion may occur.[9] The freshly precipitated hydroxide redissolves almost completely in 10 M hydrochloric acid to give a true solution of the chloro-complex. Ageing of the precipitate, however, leads to condensation and formation of higher molecular weight materials, as indicated in the diagram. This latter product is no longer soluble in hydrochloric acid, although it often suffers partial peptization. The same, or a similar product, is formed spontaneously on ageing the solution of the chloro-complex, even in 10 M hydrochloric acid. It represents the thermodynamically stable product in such systems. This product is responsible for the 260 mμ absorption band. In keeping with this model the induction period before hydrolysis and condensation takes place in acid solutions of the chloro-complex is shorter the higher the protactinium concentration.

II. COLOUR REACTIONS WITH ORGANIC REAGENTS

During recent years spectrophotometric methods of estimation of most of the transition elements of groups IV, V and VI have been reported and in many cases procedures tolerating the presence of most or even all of the other elements in this collection have been developed. The only colour reaction so far reported for protactinium is the precipitation of the orange tannate from oxalate solution, which has been used by ELSON *et al.*[10] in a separation procedure. Tracer evidence of an 8-hydroxyquinoline derivative has also been reported[6] and macroscopic amounts of the cupferrate have often been prepared in this laboratory during the purification of the element,[6] but the ready oxidation of both the latter reagent and its complex has so far dissuaded us from examining its absorption spectrum. Spectrophotometric methods of measurement would now be very convenient for checking the purity of preparations of ^{231}Pa and the following observations were made with analytical applications in mind.

A preliminary survey of a variety of promising reagents led to the following results.

Experimental

Three kinds of stock solutions of protactinium were used in the course of these experiments:
(i) The solution in hydrochloric acid referred to in Section I of this paper.

[9] Z. JAKOVAC and M. LEDERER, *J. Chromatography* **1**, 289 (1958).
[10] R. E. ELSON, G. MASON, D. F. PEPPARD, P. A. SELLERS and M. H. STUDIER, *J. Amer. Chem. Soc.* **73**, 4974 (1951).

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(ii) A solution of the complex fluoride prepared by dissolving the hydroxide in hydrofluoric acid.

(iii) A solution of the sulphate complex in about 2 N sulphuric acid, prepared by fuming down the previous solution with sulphuric acid a few times and finally diluting to 2 N in acid.

A sufficient quantity of one or other of these solutions, to produce a final protactinium concentration of 6 γ/ml, was added to 0·1 or 0·2 ml of a solution containing the organic reagent and other compounds necessary to insure the desired final pH. The experiments were conducted on microscope slides with a central depression.

Results

(a) *Methylene blue.* A saturated aqueous solution of the reagent was treated with stock solution (ii). Enough ammonium hydroxide was present to give a final pH of about 1·0. No precipitate or colour change was observed. Tantalum tested under the same conditions gave a slate-blue crystalline precipitate.[11]

(b) *Brilliant green, gentian violet and rhodamine B.* Under similar conditions these compounds gave negative results although reported to give precipitates with tantalum.[11]

(c) 1-*Nitroso* 2-*naphthol.* A solution in acetic and hydrochloric acids, 0·5 N in hydrochloric acid, was treated with stock solution (i). No precipitate or colour change was observed. Zirconium under these conditions gave a greenish-yellow precipitate.[12]

(d) *p-Dimethylaminoazobenzenearsonic acid.* A saturated aqueous solution of the acid was treated with stock solution (iii) to give a final pH 1. No precipitate or colour change was observed. Zirconium produced a precipitate under these conditions.[12]

(e) 2-*Nitroso* 1-*naphthol.* Tested as (d) with similar result. Zirconium gave a red precipitate.[13]

(f) *Alizarin.* An alcoholic solution of the reagent was added to the stock solution (iii) diluted with 0·2 N sulphuric acid. A yellow lake precipitated. Zirconium produced a lake under similar conditions.[14]

(g) *Quinalizarin.* Similar conditions to (f) gave a red lake.[14]

(h) *Morin.* Similar conditions to (f) but no lake formed. Zirconium produced a lake.[15]

(i) 8-*Hydroxyquinoline.* A solution of the reagent containing enough ammonium oxalate and oxalic acid to give a final pH of about 6 was treated with stock solution (i). A red-brown precipitate formed, which was soluble in amyl acetate. Niobium reacts similarly.[16,17]

(j) *Tannic acid.* A solution containing tannic, oxalic and sulphuric acids was treated with stock solution (iii). The final concentration of sulphuric acid was about 0·2 N. An orange precipitate was deposited, containing the protactinium. Tantalum precipitated under these conditions.[18,19]

It has been known for a long time that the polyphenols give coloured complexes

[11] M. Y. Shapiro, *J. Appl. Chem. U.S.S.R.* **11**, 1028 (1938).
[12] F. Feigl, P. Krumholz and E. Rajmann, *Mikrochimie* **3**, 395 (1931).
[13] I. Belluci and G. Savoia, *Atti. Congress Naz. Chim. Pura. Appl.* 483 (1923).
[14] H. A. Liebhafsky and E. H. Winslow, *J. Amer. Chem. Soc.* **60**, 1776 (1938).
[15] G. Charlot, *Anal. Chim. Acta* **1**, 234 (1947).
[16] J. L. Kassner, A. Garcia-Porrata and E. L. Grove, *Analyt. Chem.* **27**, 492 (1955).
[17] G. K. Belkar and V. T. Athavale, *Analyst* **82**, 630 (1957).
[18] A. R. Powell and W. R. Schoeller, *Analyst* **55**, 605 (1930).
[19] C. C. Miller and A. J. Lowe, *J. Chem. Soc.* 1258 (1940).

with many of the transition elements and these reactions are now finding analytical applications.

(k) *Pyrogallol.* An aqueous solution of the reagent was treated with stock solution (i), first in 4 N hydrochloric acid and then in a sodium sulphite–ammonium oxalate mixture at a pH above 7. The acid solution remained colourless. The alkaline solution turned yellow-brown. Under acid conditions tantalum,[20–22] titanium[23] and tungsten[23] give yellow to orange colours. In alkaline solution niobium,[21,24] molybdenum[24,25] and titanium[21] give similar colours to the protactinium complex. Zirconium did not produce any appreciable colour in either solution, even at 50 times the concentration. Vanadium[26] and cerium[26] gave blue colours.

(l) *Catechol.* Under similar conditions to pyrogallol, catechol gave a less intense yellow colour with protactinium. Previously reported colour reactions of the reagent include those with molybdenum, tungsten and vanadium,[27–29] titanium and zirconium,[30] as well as niobium and tantalum.[31]

(m) *Gallic acid.* Under the same conditions as used for pyrogallol, gallic acid gave a yellow-brown coloration with protactinium in alkaline solution. Titanium gave a similar coloration under these conditions.[32,33]

(n) *Resorcinol.* This reagent was tested under the same acid and alkaline conditions as pyrogallol but no visible colour ensued.

(o) *Tiron (catechol 3:5-disulphonic acid).* An aqueous solution of the reagent was treated with stock solution (i), both in 4 N hydrochloric acid and in an ammonium oxalate solution at pH 6. No colour or precipitate was observed. Niobium gave a yellow colour.[34] Most of the transition elements are reported to give colour reactions.[35]

Two possible colour reactions with simpler reagents have been investigated.

(p) *Hydrogen peroxide.* In a previously unreported study it was shown spectrophotometrically that solutions of protactinium in 1 or 4 N sulphuric acid containing hydrogen peroxide have no marked absorption bands between 270 and 600 mμ.[36]

(q) *Thiocyanate.* Titanium,[37] vanadium,[37] niobium[37–41] and molybdenum[42] all give coloured thiocyanate complexes. Since solvent extraction studies[3] indicated

[20] I. P. Alimarin and B. I. Frid, *Zavodskaya Lab.* **7**, 1109 (1938).
[21] M. S. Platonov and N. F. Krivoshlykov, *Trudy Vsesoyuz. Konferentsu Anal. Khim.* **2**, 359 (1943).
[22] N. F. Krivoshlykov and M. S. Platonov, *J. Appl. Chem. (U.S.S.R.)* **10**, 184 (1937).
[23] L. Ikenberry, J. L. Martin and W. J. Boyer, *Analyt. Chem.* **25**, 1340 (1953).
[24] E. C. Hunt and R. A. Wells, *Analyst* **79**, 345 (1954).
[25] J. I. Dinnin, *Analyt. Chem.* **25**, 1803 (1953).
[26] F. M. Shemyakin, *Z. Anorg. Chem.* **217**, 272 (1934).
[27] A. Martini, *An. Asoc. Quim. Argentina*, **14**, 177 (1926).
[28] A. Rosenheim, E. Hilzeimer and J. Wolff, *Z. Anorg. Chem.* **201**, 160 (1931).
[29] A. Rosenheim and C. Nernst, *Z. Anorg. Chem.* **214**, 209 (1933).
[30] A. Rosenheim, B. Raibmann and G. Schendel, *Z. Anorg. Chem.* **196**, 160 (1931).
[31] B. Sarma and J. Gupta, *J. Indian Chem. Soc.* **32**, 285 (1955).
[32] P. N. Das-Gupta, *J. Indian Chem. Soc.* **6**, 855 (1929).
[33] C. Venkateswarlu, M. Sankar Das and V. T. Athavale, *Proc. Indian Acad. Sci.* **40** A, 260 (1954).
[34] H. Flaschka and E. Lassner, *Mikrochim. Acta* 778 (1956).
[35] B. Sarma, *J. Sci. Ind. Res. (India)* **15** B, 696 (1956).
[36] J. Golden and A. G. Maddock, Unpublished work.
[37] C. E. Crouthamel, B. E. Hjelte and C. E. Johnson, *Analyt. Chem.* **27**, 507 (1955).
[38] A. A. Dobina and M. S. Platonov, *Zh. Priklad Khim.* **14**, 421 (1941).
[39] H. Freund and S. E. Levett, *Analyt. Chem.* **23**, 1813 (1951).
[40] R. J. Mundy, *Analyt. Chem.* **27**, 1408 (1955).
[41] A. Bacon and G. W. C. Milner, *Analyt. Chem.* **15**, 129 (1956).
[42] Snell and Snell, *Colorimetric Methods of Analysis* p. 383. Van Nostrand, New York (1944).

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that protactinium also forms a complex thiocyanate a spectrophotometric examination of the thiocyanate solutions was made. The same composition of solution as proposed for the spectrophotometric estimation of niobium[37] and the sulphate stock solution (iii) were used. The solution did not appear coloured nor did it show any marked absorption band between 320 and 600 mμ.

Although not yielding a specific reaction for protactinium, taken together these reactions do comprise a unique set of properties and provide means for detecting titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum and tungsten in the presence of protactinium.

Since the polyphenols gave positive colour reactions with protactinium it was decided to investigate these complexes spectrophotometrically to determine their selectivity and suitability for the spectrophotometric estimation of protactinium.

III. POLYPHENOL COMPLEXES

The qualitative experiments described above show that pyrogallol will permit the detection of tantalum in protactinium when used in acid solution. In alkaline solution protactinium, titanium, molybdenum and niobium all give brown or orange colorations.[24]

Experimental

Acid solution. Ten grammes of the phenol were dissolved in 1·5 ml of sulphuric acid and 35 ml of water. The solution was filtered and diluted to 50 ml. Four grammes of ammonium oxalate were dissolved in 100 ml of water. Five millilitres of the phenol solution were mixed with 20 ml of the oxalate solution. The appropriate amount of a stock solution of protactinium in oxalic acid was added to this mixture to produce the desired concentration. The oxalate stock was prepared by the solution of a precipitate formed by the hydrolysis of a concentrated solution of protactinium in hydrochloric acid, in oxalic acid. However, essentially the same results were obtained when the hydrochloric acid stock solution was used.

Pyrogallol, catechol and gallic acid were examined under these conditions.

Alkaline solution. Twenty grammes of hydrated sodium sulphite were dissolved in water to give 100 ml of solution. One gramme of the phenol was dissolved in 30 ml of this solution and the solution filtered and diluted to 50 ml. Four grammes of ammonium oxalate were dissolved to give 100 ml of solution. Equal volumes of each of these solutions were mixed and the appropriate amount of the stock protactinium solution in oxalic acid was added. The solutions were prepared and used immediately. The same phenols were examined.

The final protactinium concentrations were extimated by counting the α-activity of an aliquot and comparing it with a standard plutonium source, using a normal scintillation counter. A half-life of 34,000 years was assumed in calculating the concentration from the activity.

The other elements examined were dispensed from standard solutions of their complex oxalates, in the same way as the protactinium.

Measurements were made both on a Unicam and with a Carey recording spectrophotometer. In every case the measurements were made with the comparison cell containing a solution identical with the test cell except for the absence of the metal under investigation.

Results

The absorption spectra of the pyrogallol complex with protactinium in both acid and alkaline solutions are shown in Fig. 4. The absorption spectra of various concentrations of the gallic acid complex in alkaline solution are shown in Fig. 5.

The wavelengths of maximum absorption for these two complexes are estimated to be 355 and 343 mμ respectively and the molar extinction coefficients at these wavelengths are approximately $2{\cdot}6 \times 10^4$ and $5{\cdot}3 \times 10^3$.

The absorption band for the gallic acid complex lies on the edge of a strong

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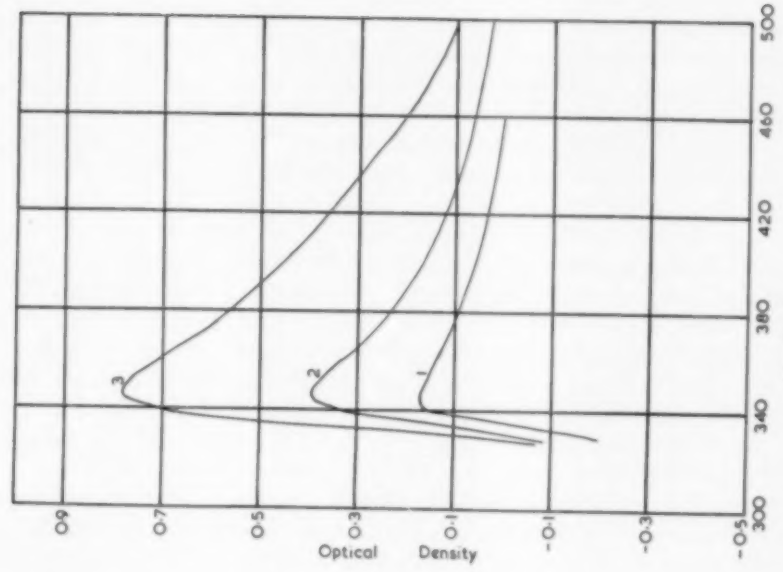

FIG. 5.—Absorption spectra of the protactinium–gallic acid complex.
1. Alkaline solution 8·2 γ ^{231}Pa/ml; 2. Alkaline solution 16 γ ^{231}Pa/ml;
3. Alkaline solution 33 γ ^{231}Pa/ml.

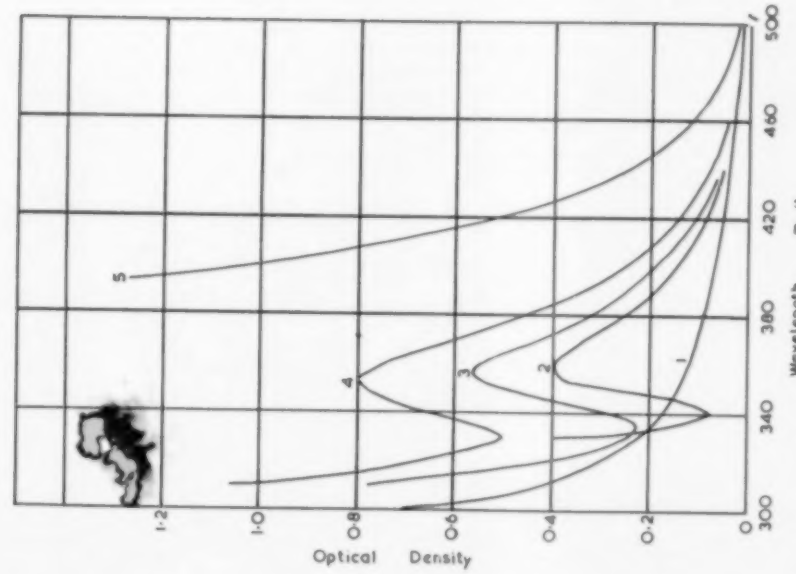

FIG. 4.—Absorption spectra of the protactinium–pyrogallol complex.
1. Acid solution 4 γ ^{231}Pa/ml; 2. Alkaline solution 4 γ ^{231}Pa/ml;
3. Alkaline solution 5 γ ^{231}Pa/ml; 4. Alkaline solution 6 γ ^{231}Pa/ml;
5. Alkaline solution 12 γ ^{231}Pa/ml.

absorption band for the blank solution. For this reason measurements below 335 mμ become difficult and inaccurate, as can be seen from the apparently negative optical densities recorded. Similar difficulties arose with the catechol complex and in this case the absorption maximum lies still closer to the absorption band of the blank. This complex showed its maximum absorption at 323 mμ with a molar extinction coefficient of $4{\cdot}8 \times 10^3$. For both these complexes the probable error in the measurements must be greater than for the pyrogallol complex. It must be recorded, however, that the spectra of both catechol and gallic acid complexes showed excellent repreducibility.

The spectra of the complexes of some of the other transition elements in the alkaline pyrogallol reagent were examined. Zirconium was not found to give any strong absorption bands between 300 and 450 mμ, nor did it interfere with the complexing of protactinium. Niobium gives a broad absorption band, without any clear maximum, stretching from about 330 to 420 mμ. The relatively sharp protactinium absorption can readily be distinguished from this plateau and the niobium can be estimated by the thiocyanate absorption. Titanium and molybdenum also interfere giving very broad absorption bands, the former with its maximum at 373 mμ and the latter at 400 mμ. In both cases the bands extend over 100 mμ and it seems likely that both elements could be estimated, or certainly detected, by measuring the absorption on the long wavelength side of the band maximum, say at 420 mμ. The protactinium band could still be distinguished in the presence of twice as much titanium. Another method of determining both titanium and niobium in the presence of protactinium will be by means of their coloured peroxy-complexes. The absence of colour in both the supernatant solution and the precipitate on depositing protactinium peroxide is a good indication of the freedom of the product from these impurities.

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J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 69 to 73. Pergamon Press Ltd. Printed in Northern Ireland

SYNTHETIC INORGANIC ION-EXCHANGE MATERIALS—III

THE SEPARATION OF RUBIDIUM AND CAESIUM ON ZIRCONIUM PHOSPHATE

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(*Received* 2 *October* 1958)

Abstract—Rubidium and caesium may be efficiently separated in macro-quantities on columns of zirconium phosphate, at loadings up to 10 per cent, by elution with solutions of ammonium salts or of nitric acid. High yields of pure materials are obtained if the separation is performed at elevated temperatures. The results are compared with those for organic resins and for other inorganic exchangers.

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THE equilibrium distribution coefficients for the alkali metals on zirconium phosphate[1] suggest that inorganic ion-exchange materials of this type may be superior to organic resins for separation of those elements, and good separations have been reported on a tracer scale on a variety of inorganic products, e.g. zirconium phosphate,[2] zirconium tungstate,[3,4] zirconium molybdate,[5] and ammonium phosphomolybdate.[6] The present paper deals with some of the factors influencing the separation of rubidium and caesium on a macro-scale on granular zirconium phosphate; in addition to possible analytical applications, this may be of interest in the separation of caesium from waste fission-products.

EXPERIMENTAL

Column sizes were either 2·5 cm × 0·6 cm diameter, containing ~1·5 g of −80 + 120 mesh granular zirconium phosphate, or 13 cm × 0·8 cm diameter containing −50 + 72 mesh material. The latter gave an optimum separation for the mesh size employed, and no improvement was obtained by further increasing the length. Columns of dimensions 37 cm × 3 cm diameter have also been used with equal success in larger scale experiments. The columns were heated by means of a vapour jacket connected to a boiler and reflux condenser, the liquids employed being acetone (b.p. 56°C), carbon tetrachloride (77°C), and ethylene dichloride (83°C).

In all cases except one the material used was taken from one batch (CE 6) prepared by Chemical Engineering Division, A.E.R.E., as described earlier;[1] there was no indication of physical or chemical breakdown after several cycles of absorption and elution. The other sample was a glassy, granular product prepared by British Drug Houses, Ltd., by a similar method. The exchanger was washed first with acid and then with water before slurrying into the column, using degassed solutions in the case of columns operating at elevated temperatures. It was normally used in the hydrogen form, but in two cases it was first converted to the sodium or ammonium form by passing several column

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[1] C. B. AMPHLETT, L. A. MCDONALD and M. J. REDMAN, *J. Inorg. Nucl. Chem.* **6**, 220 (1958).
[2] K. A. KRAUS and H. O. PHILLIPS, *J. Amer. Chem. Soc.* **78**, 694 (1956).
[3] K. A. KRAUS, T. A. CARLSON and J. S. JOHNSON, *Nature, Lond.* **177**, 1128 (1956).
[4] E. A. C. CROUCH, J. A. CORBETT and H. H. WILLIS, AERE C/R −2325 (1957).
[5] K. A. KRAUS, *et al.*, U.S.A.E.C. ORNL −2159 (1956).
[6] J. VAN R. SMIT, *Nature, Lond.* **181**, 1530 (1958).

volumes of the appropriate neutral salt solution, followed by washing with water before use. Rubidium and caesium were then absorbed in equimolar proportions by slowly percolating a small volume of solution down the column; ^{86}Rb and ^{137}Cs were used as tracers. The solution in the pore volume was then displaced with water, after which the cations were eluted with either nitric acid or ammonium salt solutions (NH_4NO_3 or $(NH_4)_2SO_4$) at linear flow rates varying between 0·5 and 1·0 cm/min. Samples of the eluate were collected for counting, either with a liquid counter or with a standard GM 4 counter and scaler; in several cases the eluate was also counted continuously by passing it

TABLE 1.—SEPARATION OF Cs AND Rb ON ZIRCONIUM PHOSPHATE: PERCENTAGE RECOVERY AND COMPOSITION OF FRACTIONS

Volume of eluate (ml)	Recovery (%)		Composition (%)	
	Rb	Cs	Rb	Cs
(a) Batch CE6, eluted with 0·5 M NH_4NO_3 at 83°C				
10·05	88·0	—	100·0	—
9·49	12·0	55·4	17·4	82·6
{305·2	—	44·6	—	100·0}*
{310·2	0·1	81·7	0·1	99·9}
(b) Batch CE6, eluted with 0·1 M NH_4NO_3 at 83°C				
{27·50	87·7	—	100·0	— }
{65·76	99·0	0·2	99·9	0·1}
17·14	1·0	5·6	15·4	84·6
{31·70	—	93·9	—	100·0}
{40·58	—	94·7	—	100·0}
(c) Batch CE6, eluted with 0·1 M HNO_3 at 83°C				
10·4	85·4	—	100·0	—
6·6	13·6	15·1	46·8	53·2
{48·9	—	60·0	—	100·0}
{57·4	1·0	84·1	1·0	99·0}
(d) BDH sample B17/10, eluted with 0·1 M NH_4NO_3 at 83°C				
55·6	97·1	—	100·0	—
11·4	2·9	0·3	88·6	11·4
{ 23·2	—	96·9	—	100·0}
{123·2	—	99·7	—	100·0}

* Bracketed values indicate alternatives

through a spiral mounted in front of a GM 4 counter connected to a type 1037A counting-rate meter and Kent recorder. Analysis for rubidium and caesium was carried out either by γ-ray spectrometry, or by counting again after 19 days (half-life of ^{86}Rb = 18·6 days).

Mass balances, based on individual samples, were within 4 per cent of the amount of material absorbed in all but three experiments, and negligible activity remained on the column. The discrepancies are probably due largely to errors in estimating the volume of the samples, and to a lesser extent to counting errors. Recoveries of materials quoted in Table 1 are based on the total recovered activity.

RESULTS AND DISCUSSION

Preliminary experiments in which only one species was absorbed on the column showed that sodium was very readily removed even with water, while rubidium was eluted efficiently with dilute acid or with dilute ammonium salts. Caesium, however, is only eluted rapidly at eluant concentrations greater than 1 M, and the most effective

eluant was found to be concentrated ammonium nitrate solution slightly acidified with nitric acid (~0·1 M). Elution with $(NH_4)_2SO_4$ at concentrations varying from 0·1 to 3 M showed the best results to be obtained with a 0·5 M solution (Fig. 1); the separation was improved by raising the temperature, with a corresponding decrease in the volume of eluate. The extent of cross-contamination decreased from 36 per cent Rb in the recovered Cs at 20°C to 3 per cent at 77°C, while the number of column volumes of eluant required to remove all the caesium was reduced from 110 to 19. More detailed studies with NH_4NO_3 as eluant showed that the partial separation

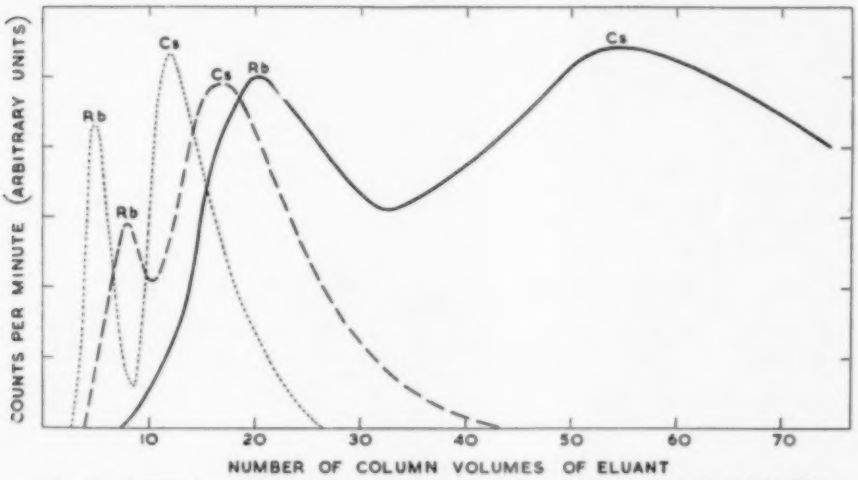

FIG. 1.—Separation of Rb and Cs on zirconium phosphate by elution with 0·5 M $(NH_4)_2SO_4$. Column 14 × 0·8 cm., containing −50 + 72 B.S.S. mesh exchanger in hydrogen form (Batch CE 6). Flow rate 1–2 ml/min; 10 per cent loading.
——— 20°C – – – – – 56°C ..... 77°C

obtained at room temperature could also be improved by reducing the loading from 10 to 1 per cent (Fig. 2), although the overlap between the peaks was still considerable, leading to low recoveries of pure material. Occasionally, a peak was observed on the continuous recording preceding that of rubidium, possibly due to a radioactive impurity present in one of the tracers; from its position and the conditions of elution it is possibly an alkaline earth nuclide.[7] No attempt was made to identify it, since it did not appear in later experiments, but from the counting results following decay it appeared to possess an appreciable half-life. When the eluant concentration was reduced to 0·1 M NH_4NO_3 the separation was improved considerably (Fig. 3); cross-contamination was greatly reduced and a much higher recovery of pure or nearly-pure materials resulted. By selecting a suitable time at which to change from dilute eluant to the concentrated strip solution, both caesium and rubidium may be recovered in high yields and high degrees of purity (Table 1). Separation on the ammonium form of the exchanger was markedly inferior to that on the hydrogen form, but the sodium form showed little difference, presumably because of the ready hydrolysis of the sodium form[1] and the low affinity of the exchanger for sodium ions. When nitric acid was used as eluant on the hydrogen form good recoveries of pure rubidium were

[7] C. B. AMPHLETT, *Proceedings of the 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Paper 271.

obtained, but caesium was removed too readily, leading to a lower recovery of pure caesium; this behaviour probably reflects differences in affinities of the exchanger for H^+ ions and for NH_4^+ ions. When the optimum conditions were applied to a separation on a sample of zirconium phosphate prepared independently (British Drug

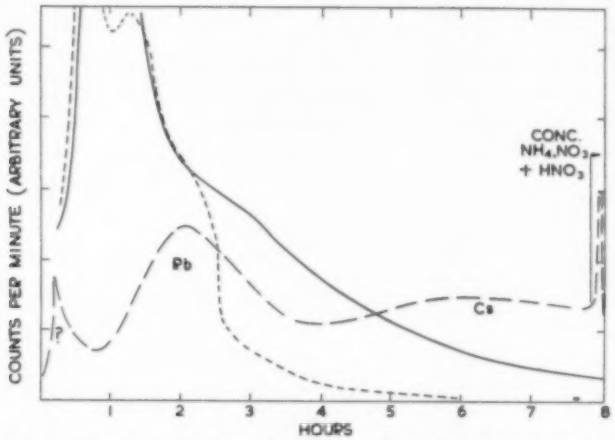

FIG. 2.—Effect of column loading and temperature on the elution of Cs and Rb from zirconium phosphate (−80 + 120 B.S.S. mesh, Batch CE 6) with 0·5 M NH_4NO_3 at 8–9 ml/hr. Column dimensions 2·5 × 0·6 cm.
———10 per cent loading, eluted at 20°C – – – – – 1 per cent loading, eluted at 20°C
.....10 per cent loading, eluted at 83°C

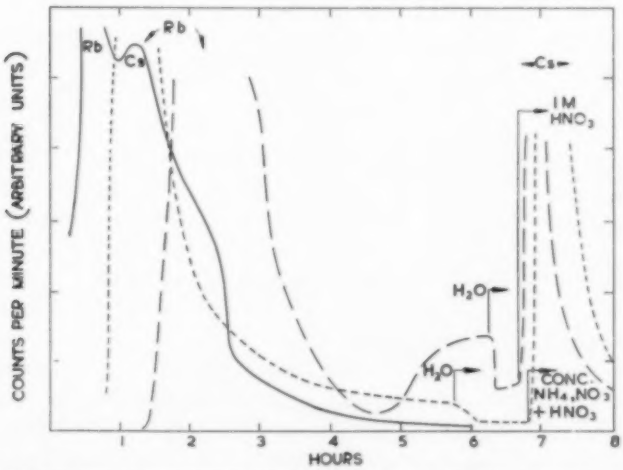

FIG. 3.—Effect of eluant concentration on the separation of Cs and Rb on zirconium phosphate (−80 + 120 B.S.S. mesh, Batch CE 6, hydrogen form) at 10 per cent loading; flow rate 8–9 ml/hr. Column dimensions 2·5 × 0·6 cm; temperature 83°C.
——— Eluant 0·5 M NH_4NO_3 – – – – – Eluant 0·1 M NH_4NO_3
.....Eluant 0·1 M HNO_3

Houses, Ltd.) a highly satisfactory separation was achieved (Fig. 4), with >97 per cent recovery of pure Rb and >99 per cent of pure Cs (Table 1).

It is instructive to compare these results with those of other workers on the separation of the alkali metals on both organic and inorganic exchangers. COHN and

KOHN[8] obtained a partial separation of Rb and Cs on Dowex-50, with considerable overlap, while KAYAS[9] obtained complete separation on Amberlite IR-100; the most satisfactory separation on an organic exchanger is that of CABELL and SMALES,[10] using Zeocarb-315. All these workers used HCl of varying strength to elute the species at linear flow-rates between 0·3 and 0·8 cm/min. The separation factor α_{Rb}^{Cs}, calculated either from individual distribution coefficients[8] or from peak volumes in the elution curves,[9,10] varies from 1·3 to 1·5; recent equilibrium determinations of K_D for the individual alkali metals on Dowex-50 from 0·1 M NH_4NO_3 give a value of $\alpha = 1{\cdot}2$.[6] When we consider the data on inorganic exchangers it is immediately

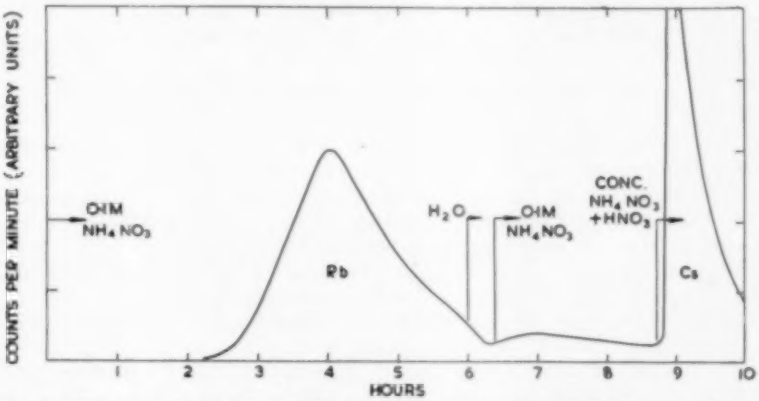

FIG. 4.—The separation of Cs and Rb on zirconium phosphate (B.D.H. sample B17/10, −80 + 120 B.S.S. mesh, hydrogen form) at 10 per cent loading. Flow rate 8–9 ml/hr, temperature 83°C.

apparent that much better separations are possible, although it would be an advantage if the rates of exchange could be improved to give a faster separation. At tracer levels it is possible to work with very small columns and relatively rapid flow-rates,[4,6] and even in the present work the column size is much reduced from those used with organic exchangers.[9,10] Where data are available it may be shown that much higher values of α are obtained, e.g. 3·1 in 0·1 M NH_4Cl,[2] and values between 3 and 5 in the present work. In the column separations which have been reported[2–5] the linear flow-rates are comparable with those in the present paper and in the work with organic resins, varying from 0·4 to 1·1 cm/min. An unusually high separation factor has been reported[6] for ammonium phosphomolybdate, where $\alpha_{Rb}^{Cs} \approx 26$, allowing separation of the alkali metals on a bed of dimensions 1·6 mm × 5 mm diameter.

The high separation factors obtainable on the inorganic exchangers offer promise of improved chemical separations, which may be carried out under conditions of temperature or ionizing radiation dose where the use of conventional organic resins is not possible.[7]

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[8] W. E. COHN and H. W. KOHN, *J. Amer. Chem. Soc.* **70**, 1986 (1948).
[9] G. KAYAS, *J. Chim. Phys.* **47**, 408 (1950).
[10] M. J. CABELL and A. A. SMALES, *Analyst* **82**, 390 (1957).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 74 to 85. Pergamon Press Ltd. Printed in Northern Ireland

THE FLUORIDES OF URANIUM—III

KINETIC STUDIES OF THE FLUORINATION OF URANIUM TETRAFLUORIDE BY FLUORINE

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Abstract—The reaction between uranium tetrafluoride and fluorine has been studied between 265° and 348°C by following the change in weight of the solid phase, using a spring balance. Formation of uranium hexafluoride at the solid surface is accompanied by migration of fluorine ions into the UF_4 lattice. The rate of production of UF_6 is in agreement with the kinetics expected for reaction between a gas and a solid at a continuously diminishing spherical interface.

The rate of reaction depends on the temperature; no reaction is detectable below 220°C. Within the limits of experimental accuracy the Arrhenius equation relates the reaction-rate constant and the temperature of reaction: the activation energies determined for three preparations of UF_4 were 15·5, 19·1 and 19·9 kcal per mole.

A linear relationship is shown to exist between the reaction rate and partial pressure of fluorine, but within the range examined the reaction rate is not affected by the velocity of gaseous reactant past the solid. The rate of UF_6 production is dependent on an "effective" surface area of UF_4, rather than the surface area determined by gaseous adsorption.

URANIUM hexafluoride can be prepared by the reaction between uranium tetrafluoride and fluorine. Before this study was made, no fundamental data on the kinetics of the reaction were available, although it was believed[1] that uranium pentafluoride was an essential intermediate in the reaction:

$$2UF_4 + F_2 \rightarrow 2UF_5$$

$$2UF_5 + F_2 \rightarrow 2UF_6$$

The present work was undertaken to elucidate the kinetics and, if possible, the mechanism of reaction.

An extensive literature exists on solid–gas reactions in which the products are solids, e.g. the oxidation of metals. Kinetic studies in which the products of reaction are entirely gaseous have been much more limited. They include work on the carbon–water,[2–5] carbon–carbon dioxide[6,7] and carbon–oxygen systems.[8,9]

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[1] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium* Pt. 1. McGraw-Hill, New York (1951).
[2] G. S. SCOTT, *Industr. Engng. Chem.* **33**, 1279 (1941).
[3] J. GADSBY, C. HINSHELWOOD and K. W. SYKES, *Proc. Roy. Soc.* A **189**, 129 (1946).
[4] F. J. LONG and K. W. SYKES, *Proc. Roy. Soc.* A **193**, 377 (1948).
[5] L. J. JOLLY and A. POLL, *J. Inst. Fuel* **26**, 33 (1953).
[6] J. GADSBY, F. J. LONG, P. SLEIGHTHOLM and K. W. SYKES, *Proc. Roy. Soc.* A **193**, 357 (1948).
[7] P. L. WALKER, R. J. FORESTI and C. C. WRIGHT, *Industr. Engng. Chem.* **45**, 1703 (1953).
[8] F. J. LONG and K. W. SYKES, *J. Chem. Phys.* **47**, 361 (1950).
[9] E. A. GULBRANSEN and K. F. ANDREW, *Industr. Engng. Chem.* **44**, 1034 (1952).

The reaction taking place at surfaces may be considered as five separate processes, the slowest of which determines the rate of reaction.[10]

(1) Transport of the reacting gas to the surface.
(2) Chemisorption of the gas.
(3) Chemical reaction at the surface.
(4) Desorption of the reaction product.
(5) Transport of the reaction product away from the surface.

In general (1) and (5) are diffusion processes; since, under the experimental conditions, only small amounts of reaction products are formed, the boundary layer will not limit access of reacting gas to the outer surface. It is thus expected that (2), (3) and (4) are the rate-determining steps: they will depend on temperature. Amongst other factors, (2) will depend on the surface area available for adsorption. The reaction studied was believed to be a surface reaction, and these factors were therefore examined, although the possibility of reaction in the solid phase was also considered.

EXPERIMENTAL

A mixture of nitrogen and a large excess of fluorine was flowed over a thin layer, a few grains thick, of uranium tetrafluoride contained in an aluminium pan. The pan was suspended from the end of a calibrated beryllium–copper spring balance in a reactor tube heated by a vapour jacket. The reaction was followed by observing changes in the extension of the spring caused by changes in weight of the contents of the pan. Fig. 1 shows the apparatus used for the majority of the work.

Beryllium–copper spring balance

A typical spring used was 2·3 cm in diameter and consisted of 40 turns of wire of 0·0076 in. diameter. It was annealed at 320°C for 4 hr and stretched taut before use. The spring sensitivity determined by the addition of weights at the ends of the glass fibre, was 0·0177 g/cm.

The effect of the column temperature on the spring sensitivity was determined. There was a spring movement of 0·014 cm per °C (which would correspond to an apparent weight change of 0·4 per cent per °C) in the range 20–35°C, under typical experimental conditions. Consequently, to obtain maximum accuracy, the spring column was jacketed and water was circulated through the jacket from a thermostat.

The spring column was made with a constriction near the botton, as shown in Fig. 1. This was to reduce the effect of convection currents set up in the reactor tube. A glass weight was suspended from the end of the spring in the reactor and the temperature of the reactor raised and lowered. The spring reading was not altered in any appreciable amount by changes of the reactor tube temperature. The accuracy of weight measurement is set by the accuracy of the cathetometer reading at a weight of 10^{-4} g or 0·1 per cent of the original sample weight.

It was found that the sensitivity of a spring did not change appreciably with time, and that the very small amount of corrosion of the spring which took place, due to diffusion of fluorine and uranium hexafluoride up the column, did not affect the accuracy of the experiments. The spring calibration was checked after every run and shown to be unchanged.

Uranium tetrafluoride

Three preparations of uranium tetrafluoride (UF_4) were used:

(i) A batch of tetrafluoride prepared by the hydrofluorination of uranium dioxide was used for most of the experimental studies. Thermogravimetry indicated that the water content was low (<0·2 per cent). Analysis, of which details are given below, showed that the material contained hexavalent uranium (4 per cent) and was low in fluorine content (22·8 per cent instead of the theoretical 24·2 per cent), indicating the presence of impurities such as uranium oxides and uranyl fluoride. The small amount of impurities does not affect the validity of the experiments, as possible weight changes of these impurities would be very small, of the order of the experimental accuracy.

[10] S. GLASSTONE, K. J. LAIDLER and H. EYRING, *Theory of Rate Processes*. McGraw-Hill, New York (1941).

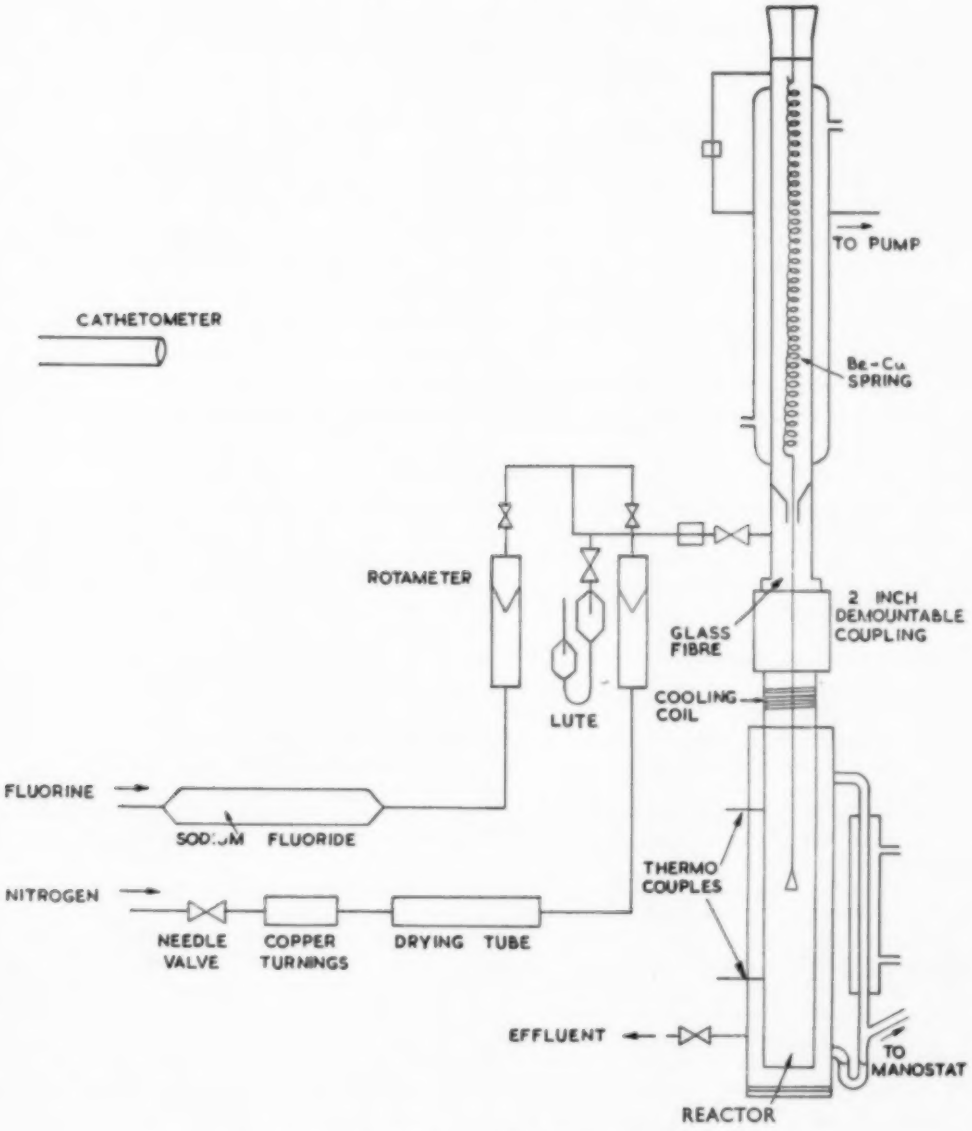

FIG. 1.—Apparatus for fluorination of uranium tetrafluoride.

(ii) Uranium tetrafluoride of large surface area was prepared by hydrating and dehydrating the tetrafluoride made by hydrofluorination. The hydrate $2UF_4 \cdot 5H_2O$ was produced by stirring material (i) in water at 20°C for five days. This hydrate was dehydrated at 270°C *in vacuo*. The product was found to be 98 per cent pure, the residual 2 per cent consisting of uranium dioxide and uranyl fluoride.

(iii) Uranium tetrafluoride of very small surface area was prepared by the sublimation of material (i) at 1000°C under high vacuum.

The surface areas of the different batches of material were determined by ethylene adsorption.[11]

[11] L. A. WOOTEN and B. G. BROWN, *J. Amer. Chem. Soc.* **65**, 113 (1943).

All the uranium tetrafluoride used was ground in a mortar before being passed through a 150-mesh sieve into an aluminium pan of diameter 1 in. By direct sieving it was found that a uniform layer a few grains thick could be obtained. From the desired spring movement and thickness of the bed, the amount of uranium tetrafluoride used in a run was fixed between 70 and 85 mg.

Method of analysis of UF_4

The total uranium content of a sample was determined using the standard method of solution in nitric acid, precipitation of ammonium diuranate and final ignition at 800–820°C to U_3O_8. The tetravalent uranium content was obtained by estimation with ceric sulphate: an excess of ceric sulphate solution was added to a weighed sample of UF_4, excess sulphuric acid added and the mixture heated to bring UF_4 into solution. On cooling, excess ceric sulphate was back-titrated against ferrous sulphate solution using N-phenylanthranilic acid as indicator. The fluorine content was determined by hydrolysis of a sample with sulphuric acid, steam distillation of the fluosilicic acid produced and estimation as lead chloro-fluoride.[12]

Fluorine supply

The fluorine was generated in an I.C.I. 60-amp electrolytic cell. The fluorine from the cell was flowed through towers packed with sodium fluoride pellets and through copper pipe to the apparatus on the bench. On the bench the fluorine was passed through a tube packed with sodium fluoride pellets and a Rotameter before entering the reactor. An overpressure-underpressure lute (see Fig 1) filled with Fluorolube (a fully fluorinated heavy oil) ensured that the cell would be subjected to only very slight suction or pressure. A Rotameter was unsatisfactory for the continuous measurement of fluorine flow rate, due to the high corrosion rate of the Rotameter tube and short-period fluctuations in the flow from the generating cell. Cell current was the most satisfactory and accurate measure of the ave age flow rate during a run; there was good agreement between the flow rate thus calculated and direct measurement with a new Rotameter (i.e. before the calibration was affected by corrosion).

The fluorine from the cell was found to be 98 per cent pure; no oxygen was detected.

Nitrogen supply

The nitrogen was the commercial material obtained in cylinders. The gas was passed through a purification train consisting of a heated silica tube packed with copper turnings at 650°C, and a drying tube containing calcium chloride and phosphorous pentoxide. The nitrogen flow rate was adjusted by a needle valve and measured with a Rotameter.

Heating the reactor

The reactor used for most of the runs was made of mild steel with the inside surface nickel plated. The reactor tube was surrounded by a vapour jacket in which mercury was boiled at a known pressure, measured by a mercury manometer and maintained by a Cartesian diver manostat. Different temperatures were obtained by varying the pressure in the vapour jacket. Two chromel–alumel thermocouples were soldered to the outside of the jacket approximately 25 cm apart; in the steady state the same temperature was registered by both thermocouples. The pan was suspended so as to move within this constant-temperature zone.

The temperature registered by the Kent recorder (to which the thermocouples were connected) was constant throughout a run and differed less than −2°C from that predicted from the mercury vapour pressure registered by the manometer. Tests with a thermocouple suspended on the inside of the reactor showed that the temperature in the reactor was within 2°C of the temperature measured by the recorder, and usually the difference was much less than 2°C.

Direct electrical heating was used in preliminary experiments, but was unsatisfactory for accurate kinetic measurements because of variation in temperature along the length of the reactor.

A typical run

Except for three runs in which the initiation temperature was determined, a fixed temperature was used throughout a run.

In a typical run the beryllium–copper spring balance was first calibrated. The uranium tetrafluoride was then sieved into the pan and its weight determined. This weight was checked by the

[12] R. Belcher and J. C. Tatlow, *Analyst*. **76**, 583 (1951).

spring balance before the uranium tetrafluoride was vacuum degassed for 3 hr at a temperature close to that of the run. The temperature of the run was fixed, and after several minutes during which constancy of temperature was ensured, the apparatus was filled to atmospheric pressure with nitrogen. Meanwhile the fluorine cell was run at the desired current and the line from the cell to the apparatus flushed through with fluorine. Cathetometer readings were taken with the column under vacuum and filled with nitrogen. The buoyancy concentration is insignificant, but an apparent increase in weight of 0·2 per cent occurs when gas flow past the pan commences. This correction remains constant throughout the run. Fluorine was then allowed to flow through the reactor, the time of opening of the tap above the fluorine Rotameter being taken as the commencement of the experimental run. Further cathetometer readings were taken at intervals throughout the run. At the end of a run the apparatus was flushed out with nitrogen before being cooled and opened to the atmosphere.

DISCUSSION OF RESULTS

(a) *Initiation temperature*

No reaction detectable by the spring balance occurs in periods of several hours at temperatures up to 220°C, but the reaction rate is measurable at 230°C.

(b) *Kinetics of reaction*

During large scale production of uranium hexafluoride it is common experience that very little hexafluoride is formed until virtually complete conversion to pentafluoride has taken place, but the experimental results of the present study show that fluorination of individual uranium tetrafluoride particles does not take place in these two distinct steps. This is deduced from the kinetic data discussed below, the first-power dependence of the rate on fluorine pressure (discussed in (f)) and the absence of any large initial increases in weight of the contents of the pan. (Any initial weight increases were very small and if intermediate fluoride was formed it could only have been formed as a surface film). The rate of hexafluoride production decreases as the fluorination of an experimental batch proceeds.

The UF_6 production rate is in agreement with the kinetics expected for reaction between a gas and a solid at a spherical interface which is continuously diminishing due to reaction with the gas. In such a reaction the following relationship can be deduced:

If the initial mass of a solid particle $m_0 = \frac{4}{3}\pi r_0^3 \rho$, where $r_0 =$ initial radius and $\rho =$ bulk density, then the rate of reduction in mass at a given temperature is assumed to be proportional to the surface area of the particle,

i.e.
$$-\frac{dm}{dt} = K4\pi r^2 \tag{1}$$

where r is the radius of the particle at time t, and K is the constant for a given temperature, partial pressure of reactant gas, and chemical reaction.

The fraction of reaction C that has taken place in time t is given by

$$C = \frac{\text{reduction in mass of particle}}{\text{initial mass of particle}} = \frac{m_0 - m}{m_0} = 1 - \left(\frac{r}{r_0}\right)^3$$

whence equation (1) becomes
$$\frac{dm}{dt} = -K4\pi r_0^2(1 - C)^{\frac{2}{3}}$$

$$\frac{dC}{dt} = \frac{1}{m_0}\frac{dm}{dt} = \frac{3K}{r_0\rho}(1 - C)^{\frac{2}{3}} = R(1 - C)^{\frac{2}{3}} \tag{2}$$

This expression is that given by ANDERSON[13] for a gas–solid reaction governed by the Law of Interface Reaction; here R is a constant equal to $r_0\rho$. Integrating expression (2), we obtain

$$(1 - C)^{\frac{1}{3}} = 1 - R't \tag{3}$$

where

$$R' = \frac{K}{r_0\rho}$$

R' is a rate constant having the units of reciprocal time. When the quantity $(1 - C)^{\frac{1}{3}}$ is plotted against t the points lie on a straight line, in agreement with equation (3),

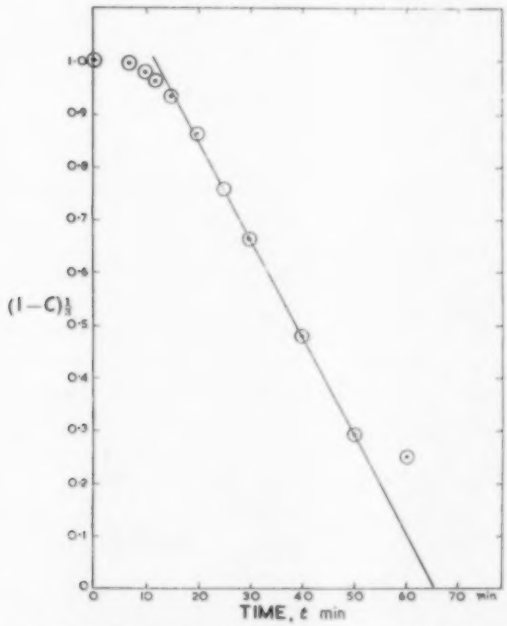

FIG. 2.—Plot of $(1 - C)^{\frac{1}{3}}$ against time at 300°C. C is fraction of the total reaction completed in time t.

except for small deviations for the first 10 per cent and last 10 per cent of the weight change at the beginning and end of the reaction. Deviation at the beginning of a run is explained by the experimental conditions used. The reactor is initially filled with nitrogen, and it takes approximately 5 min for the mixture in the reactor to become that fixed for the run. Consequently, the reaction rate at the beginning of the reaction is abnormally low. Deviation at the end of a run is discussed below.

Fig. 2 is the plot of $(1 - C)^{\frac{1}{3}}$ against t for a typical run, and Fig. 3 the uranium hexafluoride production curve based on weight loss of uranium tetrafluoride for the same run.

Attempts to fit the experimental observations to alternative mathematical models give less satisfactory agreement.

[13] J. S. ANDERSON, *Bull. Soc. Chim.* **20**, 781 (1953).

(c) *Mechanism of reaction*

In several runs when the reaction was stopped before completion it was noted that the material remaining in the aluminium pan was grey or black in colour. Closer examination showed a dark skin around the uranium tetrafluoride particles. Analysis of the residue for tetravalent uranium content confirmed an uptake of fluorine. It follows that, in addition to the principal reaction producing uranium hexafluoride, fluoride ions simultaneously diffuse into the tetrafluoride lattice. A general picture of the reaction can now be drawn.

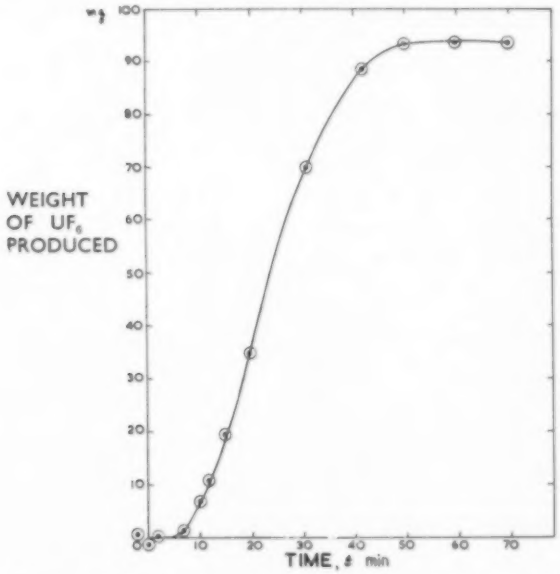

FIG. 3.—Rate of UF_6 production at 300°C. Initial weight of UF_4 (prepared from UO_2 and HF) 83 mg. Partial pressure of fluorine 220 mm.

Above the initiation temperature fluorine is adsorbed on to the surface of a uranium tetrafluoride particle and migrates into the crystal lattice, giving a non-stoicheiometric compound of variable composition richest in fluorine at the surface. Uranium hexafluoride is desorbed from the particle surface so long as the partial pressure of UF_6 in the surrounding atmosphere is less than the dissociation pressure of UF_6 for the intermediate fluoride at the surface. As reaction continues, the particle diminishes in size due to this mechanism of reaction, and the inward diffusion of fluoride ions continues so that the concentration at the centre of a particle tends to become that at the surface, the latter being determined by the partial pressure of fluorine and uranium hexafluoride at the surface.

It is stated above that there is a deviation from the expected kinetics as the fluorination nears completion. This is thought to be the result of the progressive migration of ions into the uranium tetrafluoride lattice. As reaction nears completion the concentration of fluorine at the particle centre approaches that at the surface. Whereas for the majority of the fluorination a particle consists essentially of uranium tetrafluoride with a fluorine-enriched outer surface, near the completion of reaction a phase change may occur because of the high fluorine concentration, so that the

particle becomes one of an intermediate uranium fluoride. Experiments have shown that the rate of fluorination of an intermediate fluoride made from the same UF_4 by combination with UF_6 is less than that of uranium tetrafluoride under the same conditions.

TABLE 1.—FLUORINATION OF INTERMEDIATE URANIUM FLUORIDES

UF_4 used in intermediate preparation	Intermediate fluoride subjected to F_2	Intermediate fluoride produced by F_2 uptake	Temperature of fluorination (°C)	Reaction rate constant R'	Reaction rate constant R′ calculated for UF_4
Dehydrated	$UF_{4\cdot32}$	$UF_{4\cdot52}$	300	0·00770	0·0185
Dehydrated	$UF_{4\cdot29}$	$UF_{4\cdot57}$	300	0·00530	0·0185
Hydrofluorinated	$UF_{4\cdot33}$	$UF_{4\cdot53}$	303	0·00476	0·0212
Hydrofluorinated	$UF_{4\cdot19}$	$UF_{4\cdot52}$	300	0·00435	0·0196

Intermediate fluorides were prepared from uranium tetrafluoride by the action of uranium hexafluoride at 300°C and 42 mm pressure. The apparatus was that used throughout the work (fluorination studies previously described), with the addition of a source of uranium hexafluoride. In Table 1 the experimental results are summarized and a comparison is made with the fluorination of uranium tetrafluoride. The last column in Table 1 was calculated for the fluorination of uranium tetrafluoride, assuming the dependence of fluorination rate on fluorine pressure (see section (f)).

The results show that intermediate fluorides with a composition in the region of U_4F_{17} are fluorinated up to U_2F_9 with fluorine at 300°C. Further fluorination gives UF_6. The rate of fluorination of U_2F_9 and other intermediate fluorides in this composition range is less than that of the fluorination of uranium tetrafluoride under the same conditions; the ratio of the reaction rate constants is approximately 1 : 4.

It is not possible to decide whether this change in reaction rate constant is due to a change of reaction mechanism which takes place with intermediate fluorides, or to particle growth occurring during preparation of the intermediate fluoride from the tetrafluoride (see section (e)).

In many early experiments with tray reactors, intermediate fluorides were obtained in quantity as reaction products during the fluorination of uranium tetrafluoride with fluorine. Such results are now thought to be caused by using thick layers of tetrafluoride: the concentration of fluorine is less in the lower parts of the tray, whilst the concentration of uranium hexafluoride may be high, with the consequent absorption of UF_6 and production of intermediate fluorides.

(d) *Effect of temperature*

The constant R' was determined at different temperatures using the same fluorine: nitrogen ratio and total gas flow for each type of uranium tetrafluoride. Plots of $\ln R'$ against T^{-1}, where T is in °K, were straight lines, showing that the Arrhenius relationship between the reaction-rate constant and temperature holds for this reaction.

Figs. 4, 5 and 6 are Arrhenius plots fitted by the method of least squares for the three types of tetrafluoride used. There is a considerable spread in the experimentally

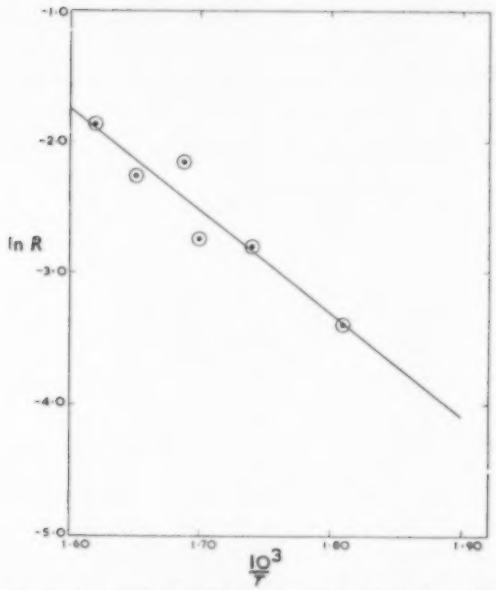

FIG. 4.—Arrhenius plot for UF_4 prepared by dehydration of $2UF_4 \cdot 5H_2O$.

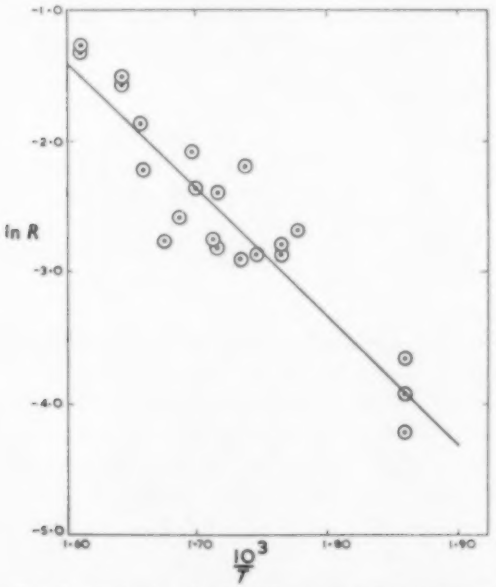

FIG. 5.—Arrhenius plot for UF_4 prepared from UO_2 and HF.

determined points, but a statistical survey of the results showed the degree of correlation in the case of uranium tetrafluoride prepared by direct hydrofluorination (with which the largest scatter was obtained) to be high, viz. −0·885. The spread of results is not surprising when one considers the non-reproducible nature of particulate solid materials. In the present work the very high heat of reaction makes temperature

control at the solid surface uncertain and is probably the principal cause of experimental scatter.

Values of R' were deduced from smoothed Arrhenius plots, and the activation energy of the reaction was deduced and is given in Table 2.

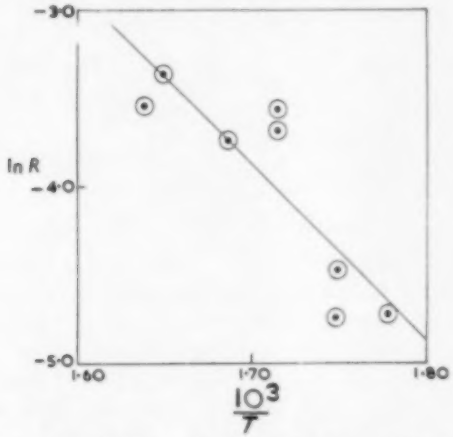

FIG. 6.—Arrhenius plot for UF_4 prepared by sublimation.

The difference in activation energy between the three materials is not large but is significant. There is an increase in activation energy with increasing degree of crystal perfection, as shown by the highest diffraction angle in a Debye–Scherrer photograph, and increased temperature of preparation.

(e) *Effect of particle size*

The constant R' of equation (3) includes r_0, the initial radius of the particle, so that a comparison of R' at the same temperature and partial pressure of fluorine for the different types of uranium tetrafluoride should show the dependence of reaction rate on the initial particle size of material. This comparison is made in Table 3.

TABLE 2.—EXPERIMENTALLY-DETERMINED ACTIVATION ENERGIES OF THE THREE PREPARATIONS OF URANIUM TETRAFLUORIDE

Type of UF_4	Temperature of preparation (°C)	θ_{max} in Debye-Scherrer photograph	Activation energy (kcal/mole)
Dehydrated	270	58°	15·5
Prepared by hydrofluorination	400	74°	19·1
Sublimed	1000	90°	19·9

In the above table, S_0 is the surface area of sublimed material and R_0 the reaction rate constant for this material. Particle size is taken as the reciprocal of surface area, in m^2/g, for comparison purposes.

The surface areas of the three types of uranium tetrafluoride were determined by ethylene adsorption, using the B.E.T. method.

TABLE 3.—EFFECT OF INITIAL PARTICLE SIZE ON RATE OF UF_4 PRODUCTION

Temperature of fluorination (°C)	Material	Temperature of preparation (°C)	Surface area, S (m^2/g)	$\frac{S_0}{S}$	R' $(min)^{-1}$	$\frac{R'}{\overline{R'}}$	$\frac{R'}{S}$ (g/m^2 min)
280	Sublimed	1000	0·021	1	0·0024	1	0·1123
280	Hydro-fluorinated	400	0·93	0·023	0·0113	0·21	0·0122
280	Dehydrated	270	2·02	0·010	0·0107	0·22	0·0051
320	Sublimed	1000	0·021	1	0·0080	1	0·3810
320	Hydro-fluorinated	400	0·93	0·023	0·0290	0·27	0·0312
320	Dehydrated	270	2·02	0·010	0·0341	0·23	0·0169

It is apparent, that the rate of uranium hexafluoride production is not directly proportional to the initial surface area as determined by gaseous adsorption. This area includes the area of channels and pores in the solid material. One might expect a surface area measured by reaction rate with fluorine not to include those pores which fluorine would only reach with difficulty by diffusion, and from which desorption of uranium hexafluoride would be slow. The sublimed uranium tetrafluoride is highly crystalline and would not be expected to be very porous, whereas the poor crystallinity of the dehydrated and hydrofluorinated materials implies a highly porous surface. These considerations satisfactorily explain the determined rates of reaction: the poorly crystalline material reacts with fluorine at a lower rate than that predicted from the surface area determined by adsorption.

Thus, although the rate of uranium hexafluoride production depends on the surface area of the tetrafluoride used, other factors, such as porosity of the material, modify the results predicted from surface areas measured by adsorption. It is therefore not sound to base predictions of reaction rate on such measurements if the temperature of preparation of the types of tetrafluoride are different; particle sizes based on Stokes' diameter measurement are more likely to be useful.

(f) *Effect of fluorine concentration*

Most of the runs were carried out with the same partial pressure of fluorine (220 mm) and total flow rate (140 cm^3/min). In several runs, however, the partial pressure of fluorine was varied, the total flow of gas being kept approximately constant. Table 4 summarizes the effect of varying the partial pressure of fluorine:—

TABLE 4.—EFFECT OF FLUORINE CONCENTRATION ON RATE CONSTANT AT 308°C FOR UF_4 PREPARED BY HYDROFLUORINATION

$F_2 : N_2$ ratio	Partial pressure (p_{F_2}) of fluorine (mm Hg)	R' (min^{-1})	$100 \times R'/p_{F_2}$
∞	760	0·0877	0·0115
1 : 1	380	0·0383	0·0105
1 : 2·5	220	0·0245*	0·0111
1 : 10	70	0·005	0·007

* Interpolated value.

There is an approximately linear relationship between reaction rate and partial pressure of fluorine for the range of partial pressures up to 760 mm.

(g) *Effect of gas velocity*

Two runs were made in which the partial pressure of fluorine was kept constant, but the total flow rate of gas was varied. The effect of this variation is shown in Table 5.

TABLE 5.—EFFECT OF GAS FLOW RATE ON RATE CONSTANT AT 311°C AND PARTIAL PRESSURE OF FLUORINE OF 220 mm (UF_4 PREPARED BY HYDROFLUORINATION)

Gas velocity (cm/min)	Total flow rate (cm^3/min)	R' (min^{-1})
12	240	0·0227
7	140	0·0265*
2·4	48	0·0217

* Interpolated value.

It is evident that the velocity of the gas has no effect on the rate of uranium hexafluoride production. It should be noted that, even with the smallest flow rate, a large excess of fluorine is present.

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THE FLUORIDES OF URANIUM—IV

KINETIC STUDIES OF THE FLUORINATION OF URANIUM TETRAFLUORIDE BY CHLORINE TRIFLUORIDE

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Abstract—The reaction between uranium tetrafluoride and chlorine trifluoride has been studied between 17° and 193°C using the same basic technique as was used in an investigation of the uranium tetrafluoride–fluorine reaction. This consists essentially of following the change in weight of the solid phase using a spring balance.

The mechanism and kinetics of reaction were shown to be substantially the same for chlorine trifluoride as fluorine. The reaction rate passes through a maximum at 105°C, falls to a minimum at 148°C and then rises again. An explanation of this unusual behaviour is suggested.

In the regions 17–58°C and 156–194°C, within the limits of experimental accuracy, the Arrhenius equation relates the reaction-rate constant and the temperature of reaction; the activation energies determined for uranium tetrafluoride prepared by hydrofluorination were 5·6 and 3·4 kcal per mole respectively. A linear relationship is shown to exist near ambient temperature between the reaction rate and partial pressure of chlorine trifluoride. In the velocity range examined, gas velocity had no effect on the reaction rate.

URANIUM tetrafluoride can be converted to uranium hexafluoride using elemental fluorine or fluorine-containing compounds such as chlorine trifluoride and cobaltic trifluoride as fluorinating agent. A kinetic study of the uranium tetrafluoride–fluorine reaction, described in Part III,[1] suggests that the principal reaction is to form uranium hexafluoride, by a direct mechanism which is accompanied by diffusion of fluoride ions into the tetrafluoride, but which does not require the complete conversion of UF_4 to U_4F_{17}, U_2F_9 or UF_5 as a necessary intermediary step. A laboratory study had been performed elsewhere (G. EDWARDS, Imperial Chemical Industries, Ltd., Widnes), in which chlorine trifluoride vapour was passed over static beds of uranium tetrafluoride. This showed that the reaction rate was temperature-dependent, rising to a peak at 110°C, but falling in the region of 175°C to a trough, and increasing again thereafter up to 500°C.

It was thought desirable to investigate this unusual variation of reaction rate with temperature, using a technique which avoided the use of thick beds of solid material. This has been done using the same basic experimental method as that described previously.[1]

The factors on which the rates of solid–gas reactions depend have been mentioned in Part III. In the present investigation the effect of temperature on reaction rate was examined in some detail. Also briefly examined were the effects of the concentration of gaseous reactant close to the solid surface and of gas velocity. The experimental

[1] Part III: V. Y. LABATON and K. D. B. JOHNSON, *J. Inorg. Nucl. Chem.* **10**, 74 (1959).

conditions were such that diffusion was not the limiting factor determining the gas concentration at the solid surface, and the partial pressure was a measure of the effective concentration of gaseous reactant.

EXPERIMENTAL

General

A mixture of nitrogen and chlorine trifluoride in considerable excess was flowed over a thin layer, a few grains thick, of uranium tetrafluoride contained in an aluminium pan. The pan was suspended from the end of a calibrated beryllium–copper spring in a reactor tube heated by a vapour jacket. The reaction was followed by observing changes in weight of the contents of the pan.

The apparatus used was in the main identical with that described in Part III.[1] The source of chlorine trifluoride was a cylinder connected to a valve and a tube packed with sodium fluoride. Pressure gauges (Kelvin and Hughes, Ltd.) were included in the nitrogen and chlorine trifluoride lines after the Rotameters. All taps and glass tubing in the original apparatus in contact with undiluted chlorine trifluoride were replaced by metal valves (Paterson Engineering Co.) and copper tubing.

The following description omits details already given in Part III, and only emphasizes the important features of the experimental work, particularly where they differ from those of the fluorine study.

Uranium tetrafluoride

A batch of material prepared by the action of anhydrous hydrofluoric acid on uranium dioxide was used throughout. The water content was low (0·2 per cent); the hexavalent uranium (4 per cent) and low fluorine content (22·8 per cent instead of the theoretical 24·2 per cent) indicated the presence of small amounts of impurities, probably uranium oxides and uranyl fluoride. Possible weight changes of these impurities would be very small and of the order of the experimental accuracy.

The tetrafluoride was ground before use and sieved (150 mesh) directly into an aluminium pan, 1 in. in diameter. A uniform layer a few grains thick was so obtained. To obtain a convenient spring movement and thickness of bed, 65–85 mg of UF_4 were used in a run.

Chlorine trifluoride

The chlorine trifluoride used was taken directly from a cylinder obtained commercially. It is known that hydrogen fluoride is the chief impurity present, and this was removed by passing the gas stream through a tube packed with dry sodium fluoride pellets. The flow rate was measured directly with a Rotameter, which functioned satisfactorily for several runs before replacement, provided that air and nitrogen which might contain trace impurities were excluded. Back-diffusion of nitrogen was reduced to a minimum by maintaining the pressure of chlorine trifluoride slightly in excess of the nitrogen pressure. The minimum flow, adopted for the majority of the runs, was such that chlorine trifluoride was in a six-fold excess at the highest reaction-rate.

Heating the reactor

The reactor was surrounded by a vapour jacket in which different materials were boiled under atmospheric and reduced pressure. In order to cover the temperature range examined, chloroform, *n*-amyl methyl ketone and naphthalene were used in the vapour jacket. In the steady state, the same temperature was registered by the two thermocouples which were soldered to the outside of the jacket, about 25 cm apart. The pan was suspended so as to move within the constant-temperature zone.

A typical run

In a typical run the beryllium–copper spring was calibrated before use. The weight of pan and uranium tetrafluoride was determined on an analytical balance and checked by the spring balance. The uranium tetrafluoride was vacuum-degassed for three hours at a temperature close to that of the run. When the temperature of the run had been fixed, the apparatus was filled to atmospheric pressure with dry nitrogen, except for the chlorine trifluoride supply system. The time at which chlorine trifluoride flow began was taken as the commencement of a run, although it was apparent

from extrapolation of the reaction-rate curve that the chlorine trifluoride took several minutes to reach the uranium tetrafluoride.

In runs at low temperatures, the change in weight of the contents of the pan was followed by cathetometer readings taken at intervals throughout the run. In high-temperature runs, when reaction was complete in a few minutes, the cathetometer was replaced by a telescope containing a graticule. The fluorination was then followed by noting the times at which the "pointer" on the spring, moving down the field of vision, passed the fixed marks of the graticule.

This, incidentally, suggests a possible technique of general application to fast gas–solid reactions, a ciné-camera being used to record the field of view in the telescope.

At the end of a run the apparatus was flushed out with nitrogen, and finally the whole apparatus as far as the cylinder valve was evacuated.

DISCUSSION OF RESULTS

(a) *Initiation temperature*

The reaction rate was measurable at room temperature.

(b) *Kinetics of reaction*

At temperatures above 150°C the solid material undergoing fluorination did not increase in weight at all. At lower temperatures the weight increase was always less than that required for complete conversion of UF_4 to U_4F_{17}. Volatile uranium hexafluoride therefore begins to form before conversion of tetrafluoride to a higher fluoride is complete (see Fig. 2).

The UF_6 production rate is in agreement with the kinetics expected for reaction between a gas and a solid at a spherical interface which is continuously diminishing due to reaction with the gas. For such a reaction the following relationship can be deduced:

$$(1 - C)^{1/3} = 1 - R't$$

where C is the fraction of the total reaction completed in time t,

R' is a rate constant having the units of reciprocal time.

When the quantity $(1 - C)^{1/3}$ is plotted against t, the points lie on a straight line in agreement with the equation, except for small deviations for the first 10 per cent and last 5 per cent of the weight change at the beginning and end of the reaction, respectively. Deviation at the beginning of the reaction is explained by the experimental conditions, 1–2 min being required for the proportions of the gaseous mixture in the reactor to become those fixed for the run; the reaction rate at the beginning of the reaction is thus abnormally low The end deviation can be explained by a consideration of the mechanism of reaction.[1]

Fig. 1 is the plot of $(1 - C)^{1/3}$ against t for a typical run, and Fig. 2 the uranium hexafluoride production curve based on weight loss of uranium tetrafluoride for the same run.

(c) *Effect of chlorine trifluoride concentration*

In all the runs at elevated temperatures, the partial pressure of chlorine trifluoride was maintained at 39 mm and the total gas flow rate at 158 cm^3/min. In two runs at ambient temperature the partial pressure was varied, the total flow of gas being kept approximately constant. Table 1 summarizes the effect of this variation.

The results obtained indicate an approximately linear relationship between

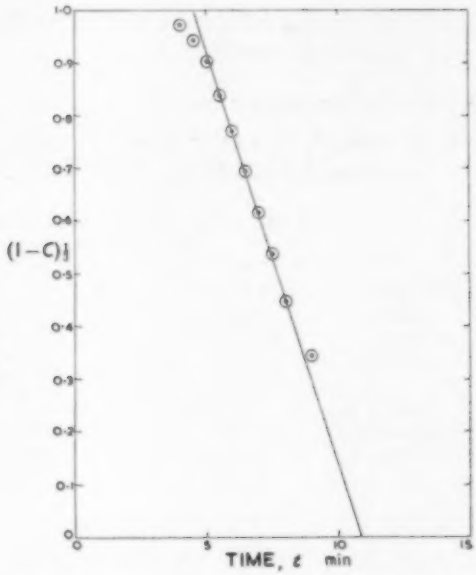

FIG. 1.—Plot of $(1 - C)^{1/3}$ against time at 139°C. C is fraction of the total reaction completed in time t. Initial weight of UF_4 = 64 mg, partial pressure of ClF_3 = 39 mm, gas velocity = 8 cm/min.

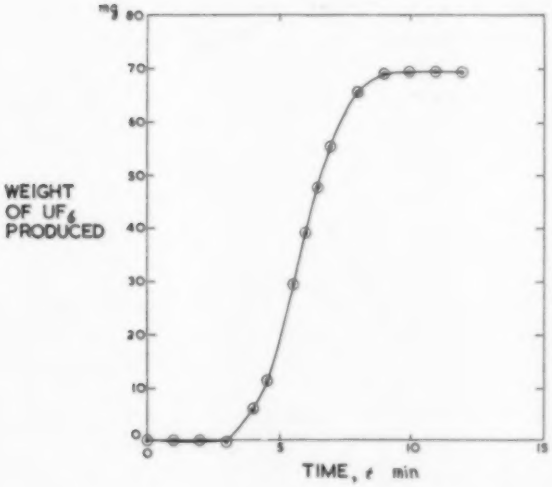

FIG. 2.—Rate of UF_6 production at 139°C. Initial weight of UF_4 = 64 mg, partial pressure of ClF_3 = 39 mm, gas velocity = 8 cm/min.

TABLE 1.—EFFECT OF CHLORINE TRIFLUORIDE CONCENTRATION ON RATE CONSTANT FOR UF_4 PREPARED BY HYDROFLUORINATION

Partial pressure of ClF_3 (mm Hg)	Temperature (°C)	R' (min^{-1})	$10^3\ R'/P_{ClF_3}$ (mm^{-1} min^{-1})
57	17·5	0·114	2·00
39	17·5	0·071*	1·82
74	21·0	0·142	1·91
39	21·0	0·075*	1·92

*Interpolated values from Fig. 3.

reaction rate and partial pressure of chlorine trifluoride within the narrow temperature and pressure range examined.

(d) *Effect of gas velocity*

In several runs the total flow rate of gas was varied, the partial pressure of chlorine trifluoride being kept constant. The effect of this variation is shown in Table 2, in

TABLE 2.—EFFECT OF GAS FLOW RATE ON RATE CONSTANT
(PARTIAL PRESSURE OF ClF_3 = 39 mm)

Total flow rate (cm^3/min)	Reaction rate constant R' (min^{-1})	Temperature of reaction (°C)	Rate constant at 20°C R'_{20} (min^{-1})	Gas velocity (cm/min)
99	0·0719	18·5	0·0781	4·9
126	0·0877	23·0	0·0751	6·3
158	0·0780	20·0	0·0780	7·9
172	0·1205	29·0	0·0762	8·6

which the gas velocity has been estimated from the flow rate and dimensions of the apparatus. Since the runs were carried out at different temperatures, a "corrected" reaction rate constant R'_{20} has been calculated from the Arrhenius plot for each flow rate.

It is clear that, in the velocity range 5–8·8 cm/min, gas velocity has little or no

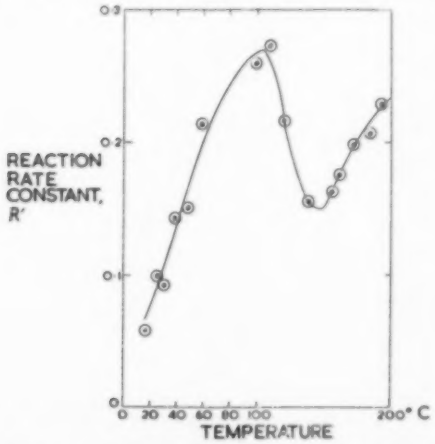

FIG. 3.—Plot of reaction-rate constant R' against temperature.

effect on the reaction rate; variations in the reaction rate constant due to change of gas velocity are within the experimental error.

(e) *Effect of temperature*

The reaction-rate constant, R', was determined at different temperatures using the same partial pressure of chlorine trifluoride (39 mm Hg) and the same total gas flow-rate (158 cm^3/min). Fig. 3 is a plot of R' against temperature. The reaction

rate passes through a maximum at 105°C, falls to a minimum at 148°C and then rises again.

In considering the kinetics of the solid-gas reaction and in particular the variation of rate with temperature, three models were considered. In the first model, the initial uranium tetrafluoride particle is assumed to form during fluorination a layer or skin of intermediate fluoride UF_{4+x}, in which $0 < x < 1$ with x greatest at the surface and initially zero at the centre of the particle. It is believed that x can have values between 0 and 0·25, or can be 0·5 or 1·0, corresponding with solid solutions between UF_4 and U_4F_{17}, and with U_2F_9 or UF_5, respectively. There is no evidence for the existence of a continuous range of non-stoicheiometric intermediate fluorides above U_4F_{17}. The value of x is known (from X-ray crystallographic studies of the residual solid just before complete conversion to hexafluoride) to rise above zero at the centre in the later stages of reaction. The second model assumes a layer or skin of a distinct stoicheiometric intermediate fluoride, U_4F_{17}, U_2F_9 or UF_5, with a sharp boundary between the phases. The third model assumes that during fluorination the particle has distinct but irregular sections of uranium tetrafluoride and intermediate fluoride, the latter growing from one or two nucleation sites. From the evidence presented in Part III and this paper, the first model is believed to represent the facts most closely. Models analogous to these have been discussed for oxidation of uranium dioxide.[2,3]

In the present case the picture is complicated compared with the oxide system by the facts that uranium hexafluoride—the final fluorination state—is volatile, and a back-reaction of hexafluoride with lower fluorides is possible. All or any of the following steps may occur:

(i) diffusion of ClF_3 to the solid surface.
(ii) adsorption of ClF_3 on the surface.
(iii) chemical reaction $UF_4 \rightarrow UF_6$.
(iv) chemical reaction $UF_4 \rightarrow UF_{4+x}$.
(v) chemical reaction $UF_{4+x} \rightarrow UF_6$.
(vi) desorption of UF_6.
(vii) diffusion of UF_6 away from the surface.
(viii) recombination of UF_6 with UF_{4+x} at the surface.

At the lowest temperatures studied, physical adsorption of ClF_3 would be expected to occur on the surface. No data are available for the adsorption of chlorine trifluoride on uranium tetrafluoride, but for many systems a monolayer is obtained when the ratio of the partial pressure to the saturation vapour pressure is about 0·1. This occurs at 5°C under the present conditions. At higher temperatures the surface coverage would be partial and tending toward a linear (Langmuir type) adsorption isotherm, consistent with the observation that reaction rates near the ambient temperature have first-order dependance on the partial pressure of chlorine trifluoride. At still higher temperatures, in particular at temperatures above the critical temperature of chlorine trifluoride (150°C), extensive physical adsorption becomes impossible The fall in reaction rate constant at temperatures between 100°C and 150°C may be qualitatively ascribed to the transition from physical adsorption to chemisorption of

[2] S. Aronson, R. B. Roof, Jr. and J. Belle, *J. Chem. Phys.* **27**, 137 (1957).
[3] K. B. Alberman and J. S. Anderson, *J. Chem. Soc.* S.303 (1949).

chlorine trifluoride. The desorption of chlorine trifluoride is assumed to have a greater effect on the reaction rate than the increase in kinetic energy of the molecules. It has not been possible to interpret this hypothesis mathematically.

A more likely explanation of the effect of temperature on rate constant lies not in step (ii) above but in steps (iv) and (v)—the reactions to form UF_{4+x} and its subsequent fluorination to UF_6. The activation energies for diffusion processes in gases are generally very small, and it is known that gaseous diffusion rates vary with the square of the absolute temperature, whereas the rate of fluorination varies exponentially with the temperature. It is therefore highly improbable that stages (i) or (vii) are rate-controlling. The fluorination with fluorine to form uranium

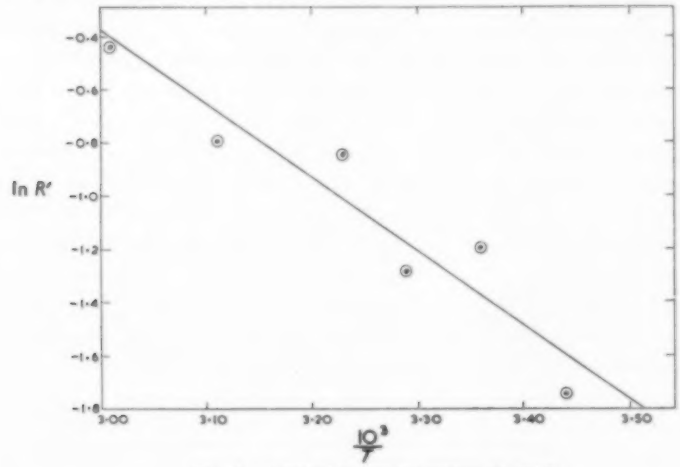

FIG. 4.—Arrhenius plot for region 16–60°C.

hexafluoride occurs at measurable rates only at temperatures above 220°C. At this and higher temperatures intermediate fluorides with $x \geqslant 0{\cdot}25$ are not stable if the partial pressure of uranium hexafluoride is less than 0·02 mm Hg.[4] In the work described in Part III stoicheiometric intermediate fluorides, viz. U_4F_{17} etc., are not expected to be stable during the early stages of fluorination because of the conditions obtaining. At the lower temperatures at which chlorine trifluoride reacts, intermediate fluorides with $x \geqslant 0{\cdot}25$ are more easily formed. At temperatures below 100°C, the migration of fluoride ion through the UF_4 lattice is very slow, and plays a relatively unimportant part. At temperatures above 100°C the incorporation of additional fluoride ions in a surface layer can probably begin. Other work at this laboratory on the reaction of UF_6 with UF_4 has shown that penetration of fluoride ion throughout the grain is temperature and pressure dependent, and from the results one would only expect very slow penetration with low UF_6 pressures below 100°C. It is known[1] that the fluorination of intermediate fluorides is slower (by about a factor of 4) than the fluorination of the tetrafluoride, for reasons probably not connected with grain size or surface area. The lower rate constants between 100° and 150°C can therefore be ascribed to the lower reaction rate of chlorine trifluoride with a UF_{4+x} surface than with a UF_4 surface. Production of UF_6 by steps (iii) and (v)

[4] P. AGRON. *U.S.A.E.C. Report AECD* 1878 (declassified 1948).

and formation of intermediate fluoride, step (iv), are both expected to depend on the surface area of the particles undergoing fluorination, and in fact the $(1 - C)^{1/3}$ relationship as expected is followed throughout the temperature range. At temperatures above 150°C the reaction passes into a range where intermediate fluorides are not stable and therefore do not form.

This explanation accords with the observations that initial weight increases occurred in the present experiments only at temperatures below 150°C. The data obtained in the present experiments do not enable a distinction to be drawn between this explanation and one based on formation of UF_6 and its subsequent recombination with the solid by step (vii) above, but in a flowing system the necessary steady-state local concentrations of uranium hexafluoride vapour seem unlikely to arise.

Fig. 4 shows the variation of ln R' with temperature plotted to follow the Arrhenius relationship, in the range 15–58°. The apparent activation energy in this range is 5·6 kcal per mole. A similar plot in the range 156–194°C shows the Arrhenius relationship to hold, and the deduced energy of activation is 3·4 kcal per mole.

(f) *Comparison with fluorination by fluorine*

A comparison of the results obtained in this study and those obtained previously for the uranium tetrafluoride–fluorine reaction[1] shows that fluorination with chlorine trifluoride proceeds at a much lower temperature than that with fluorine. The activation energy is also much lower, that for the uranium tetrafluoride–fluorine reaction being 19·1 kcal per mole for the same solid material. The relative magnitude of the reaction rates with fluorine and chlorine trifluoride was obtained by extrapolation of the plot in Fig. 3 to 265°C. The reaction-rate constants were compared, correcting for the difference in partial pressure of the runs: the fluorination by chlorine trifluoride is 160 times faster than that by fluorine (at 265°C). It is probable, however, that the difference between the reaction rates would be smaller at higher temperatures, as the reaction rate with fluorine increases rapidly with temperature, whereas that with chlorine trifluoride shows a less rapid increase in the region above 170°C.

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The author wishes to thank Mr. K. D. B. Johnson for helpful discussions.

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KINETICS OF THE OXIDATION OF CERIUM(III) BY CONCENTRATED NITRIC ACID*

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Abstract—The oxidation of Ce^{III} by concentrated nitric acid solutions has been shown to be a reversible reaction. The kinetics for the oxidation at 90–110°C in 12–16 N HNO_3 were studied by a procedure in which volatile oxides of nitrogen were swept away by inert gas. The kinetics were consistent with an electron transfer reaction between Ce^{III} and NO_2^+, first order in each reactant. An overall activation energy for the process of 8 kcal was indicated.

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WHEN a mixture of rare earth nitrates is dissolved in concentrated nitric acid, a portion of the cerium(III) is oxidized to cerium(IV). BARBIERI[1] reported that the action of nitric acid on a solution of rubidium and cerium(III) yielded rubidium hexanitratocerate(IV) in a 33 per cent yield. VICKERY[2] has mentioned this oxidation in the separation of the ammonium and magnesium double rare earth nitrates. However, he noted that when the double cerium(IV) nitrates are deliberately crystallized out as the head fraction, a partial reduction to the cerium(III) salt occurs when the fractions are heated above 60°C.

Since cerium(IV) is known to be more extractable into organic solvents[3,4] than cerium(III), the solvent-extraction separations of rare earths are influenced by the relative proportions of the two oxidation states. The present study was intended to determine the stability of cerium(IV) in concentrated nitric acid and to provide quantitative information concerning the kinetics of its formation from cerium(III).

In view of uncertainties in the species for the two oxidation states of cerium in the nitric acid media, the overall reaction is written as:

$$Ce^{III} + H_3O^+ + HNO_3 \rightarrow Ce^{IV} + NO_2 + 2H_2O. \quad (1)$$

Lower oxides of nitrogen are not expected in appreciable quantities in the presence of the powerfully oxidizing Ce^{IV}. The standard oxidation potentials indicate a negligible oxidation of Ce^{III} by nitric acid under the unit activity conditions. Therefore, it is expected that in a closed system the reverse of reaction (1) leads to the establishment of a steady state condition. Formation of NO_2 by spontaneous decomposition of nitric acid is also a possibility.

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2. \quad (2)$$

Therefore, such decomposition of HNO_3 leads to a reduction of cerium(IV). With its high volatility, NO_2 can be lost from a solution to permit substantial oxidation

* Contribution No. 644. Work performed in the Ames Laboratory of the Atomic Energy Commission.

[1] G. A. BARBIERI, *Atti Accad. Lincei.* **16,** 395 (1908).
[2] R. C. VICKERY, *Chemistry of the Lanthanons* p. 115. Butterworths Scientific Publications, London (1953).
[3] J. C. WARF, *J. Amer. Chem. Soc.* **71,** 3257 (1949).
[4] L. IMRE, *Z. Anorg. Chem.* **164,** 214 (1927).

of the cerium(III). An inert gas was bubbled rapidly through the solutions to sweep out NO_2 so the kinetics of the forward reaction in equation (1) might be followed.

EXPERIMENTAL

Materials. Lindsay Chemical Company Code 270 cerium(III) nitrate was used. The ammonium hexanitratocerate(IV) used was obtained from the G. Frederick Smith Chemical Company. Cerium (IV) solutions, used for stability tests, were prepared by dissolving hydrous cerium(IV) oxide in nitric acid. For the preparation of the hydrous cerium(IV) oxide, ammonia was added to a cerium(III) nitrate solution to precipitate the hydroxide. To the slurry of cerium(III) hydroxide was added hydrogen peroxide in excess. The precipitate was filtered, washed with water, and dried at 100°C to give the hydrous cerium(IV) oxide.

Reagent grade concentrated nitric acid and other chemicals which were used met the ACS specifications.

Analyses. For the determination of nitric acid concentrations, cerium was first precipitated by the addition of potassium hexacyanoferrate(II). The solution was then titrated with standard NaOH; the end-point was determined potentiometrically by means of a Beckman model M pH meter.

The total cerium in solution was determined by the bismuthate method.[5] A spectrophotometric procedure, employing a Beckman model DU spectrophotometer, was utilized to determine the cerium(IV) concentrations. Standard solutions of cerium(IV) for calibration of the procedure were prepared from both hydrous cerium(IV) oxide and ammonium hexanitratocerate(IV), whose cerium (IV) content had been determined by analysis. Weighed quantities of these materials were dissolved in nitric acid solutions of various concentrations. The molar absorptivity of cerium(IV) was therefore determined over a range of cerium(IV) and nitric acid concentrations at wavelengths of 500 and 520 mμ. In accordance with the results of WYLIE[6] the molar absorptivity did not change with nitric acid concentration in the range 8–11 molar nitric acid. However, a small but real change in the molar absorptivity between 11 and 15·6 molar nitric acid was noted. For analyses at any given nitric acid concentration, the molar absorptivity of Ce^{IV} was interpolated from the values for the standard solutions. The molar absorptivity varied reversibly over a temperature range of 25–40°C. Therefore, the temperature of the spectrophotometer was controlled at 25·0 ± 0·2°C. These observations imply a change in the nature of the solvation of cerium(IV) in the concentrated nitric acid solutions which deserves further study.

Procedure. The reaction vessel was a 500 ml round bottom Pyrex flask to which a water-cooled condenser was attached by a standard taper. By means of a stopcock above the condenser the system could be open to or closed from the atmosphere. The sweeping gas was introduced below the liquid level through a glass tube which was sealed through the glass wall. A second side arm, provided with a stopcock and a squeeze bulb, permitted the removal of samples for analysis through the gas inlet tube. Nitrogen gas, metered by means of a calibrated rotameter, was passed through a copper coil in the thermostat bath into the reaction flask and out through the condenser to a hood. The thermostat was an oil bath, controlled to ±0·2°C in the range, 90 to 120°C.

A reaction flask, containing nitric acid, was allowed to come to thermal equilibrium in the thermostat. At zero time, the cerium was introduced either as solid cerium(III) nitrate hexahydrate or in a small volume of water. Immediately, the condenser was attached and the nitrogen flow was started. After various intervals the gas flow was interrupted just long enough for the withdrawal of samples. The samples were placed in an ice bath to quench the reaction. They were subsequently analysed for acid content, cerium(IV), and total cerium.

RESULTS AND DISCUSSION

In a preliminary investigation an oxidation at 100°C was attempted under static conditions. The amount of cerium(IV) which was formed was inappreciable, and brown fumes of NO_2 were observed in the flask. With a flow of inert gas the NO_2 was removed and higher yields of cerium(IV) were attained. The formation of cerium(IV) was initially very rapid, but the reaction rates decreased very quickly and conversions

[5] G. F. SMITH, *Cerate Oxidimetry* p. 48. G. Frederick Smith Chemical Co., Columbus, Ohio (1942).
[6] A. W. WYLIE, *J. Chem. Soc.* 1474 (1951).

greater than 35 per cent were never obtained with the highest flow rates practicable, ca. 200 l/hr.

Stability of cerium(IV). SMITH[7] has observed a reduction of cerium(IV) solutions which increased with the HNO_3 concentration up to 4 N HNO_3 at 100°C. In one static stability test at 120°C in 15·6 N HNO_3 with 0·151 mole/l. Ce^{IV} and 0·025 mole/l. Ce^{III}, it was observed that 13 per cent of the Ce^{IV} was reduced in 8 hr. In another test at 100°C with a solution, initially 0·120 molar in Ce^{IV} (100%) and 15·2 N in HNO_3, a gas flow of 131 l/hr was maintained. Reduction of cerium in this test was not detected in an 8 hr period, during which the concentration of nitric acid fell to 14·6 N as a consequence of evaporation. A solution of pure cerium(IV) can be stable in nitric acid solutions for a long period, providing there is moderate gas sweeping.

Kinetics of oxidation of cerium(III). With the high gas flow through the solutions and the elevated temperatures used in the present work, the volume of the solution decreased since the condenser failed to return all of the vapours to the reaction vessel. The concentrations of Ce^{IV} and total Ce were plotted against time. Rates of change of these concentrations were determined graphically from the slopes of these curves. In a conventional kinetics study, the volume of solution does not change appreciably and the reaction rate is expressed as the rate of change in concentration. However, the rate of the chemical reaction properly must represent $(1/V)(dN_4/dt)$ where V is the volume and N_4 is the number of moles of Ce^{IV}. The rate of change of the concentration of cerium(IV), $[Ce^{IV}]$, is given by equation (3).

$$d[Ce^{IV}]/dt = (1/V)(dN_4/dt) - N_4(1/V^2)(dV/dt) \tag{3}$$

Since the concentration of total cerium, $[Ce_T]$, equals N_T/V where N_T is a constant,

$$d[Ce_T]/dt = -(N_T/V^2)\,dV/dt = -([Ce_T]/V)\,dV/dt. \tag{4}$$

From equations (3) and (4) the rate of reaction is given by the expression,

$$(1/V)(dN_4/dt) = d[Ce^{IV}]/dt - ([Ce^{IV}]/[Ce_T])(d[Ce_T]/dt). \tag{5}$$

Rates of reaction were calculated from the slopes of the measured concentrations by means of equation (5).

Although reaction rates were determined with satisfactory accuracy, the evaporation of solvent was especially troublesome because solutions of high concentrations of nitric acid lost HNO_3 more rapidly than H_2O. The concentration of nitric acid decreased during the experiment, and rates were strongly dependent upon the nitric acid concentrations. However, in the nitric acid range of 12·0 N to 13·8 N, the evaporation occurred without significant changes in nitric acid concentration over a period of 8–10 hr. Results of three kinetics experiments at constant nitric acid concentrations in this range are shown in Fig. 1 in which the cerium(III) concentration, $[Ce^{III}]$, divided by the reaction rate was plotted against $[Ce^{IV}]$. The plots show an exceptionally high order dependence of the reaction rate on the nitric acid concentration. Thus the intercepts of the curves decrease by a factor of about 4·0 as the nitric acid concentration increases only from 12·0 molar (mole fraction 0·270) to 13·75 molar (mole fraction 0·318).

This extreme dependence upon HNO_3 content can be explained if the active oxidizing agent is NO_2^+, the species which is believed also to effect the nitration of

[7] G. F. SMITH, *Cerate Oxidimetry* p. 14. G. Frederick Smith Chemical Co., Columbus, Ohio (1942).

organic compounds. The rate-determining step becomes the electron transfer reaction:

$$Ce^{III} + NO_2^+ \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Ce^{IV} + NO_2. \quad (6)$$

The difference in the geometrical shape between the NO_2 molecule and the nitronium ion provides a barrier in addition to the solvation differences in the two states of cerium.

It is also apparent from the plots in Fig. 1 that reaction rates fell off as Ce^{IV} was formed. The decrease in rate as the cerium(IV) concentration increases may reflect

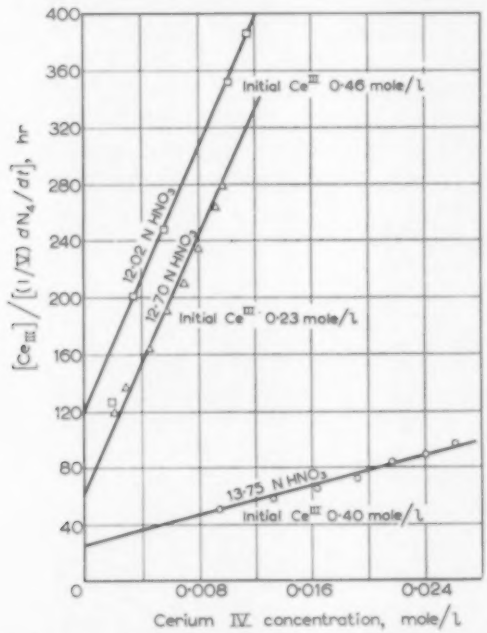

FIG. 1.—Rate dependence for the oxidation of cerium(III) by nitric acid. Temperature 100°C, nitrogen sweeping-gas flow-rate 131 l/hr.

the fact that the gas flow does not sweep out the volatile NO_2 sufficiently to prevent completely the reverse reaction of equation (6). If the forward and reverse reactions of equation (6) are first order in each reactant and if the loss of NO_2 to the gas stream is proportional to its concentration in solution, the overall rate of formation of NO_2 is given by the equation,

$$(1/V)\, dN_{NO_2}/dt = k_1[Ce^{III}][NO_2^+] - k_{-1}[Ce^{IV}][NO_2] - k_2[NO_2] \quad (7)$$

where N_{NO_2} represents the total moles of NO_2. Likewise, the rate of formation of Ce^{IV} is

$$(1/V)\, dN_4/dt = k_1[Ce^{III}][NO_2^+] - k_{-1}[Ce^{IV}][NO_2]. \quad (8)$$

Under the conventional assumption of a condition for which $[NO_2] \ll [Ce^{IV}]$, and therefore $dN_{NO_2}/dt \ll dN_4/dt$, the concentration of NO_2 is,

$$[NO_2] = k_1[Ce^{III}][NO_2^+]/(k_{-1}[Ce^{IV}] + k_2). \quad (9)$$

The rate of formation of Ce^{IV} becomes

$$\left(\frac{1}{V}\right)\frac{dN_4}{dt} = k_1[Ce^{III}]\Big/\left(\frac{k_{-1}[Ce^{IV}]}{k_2[NO_2^+]} + \frac{1}{[NO_2^+]}\right). \qquad (10)$$

The straight line relation for the plots of

$$[Ce^{III}]/(1/V)\, dN_4/dt \text{ vs. } [Ce^{IV}]$$

predicted by equation (10), is clearly evident in Fig. 1. According to equation (10), intercepts of the straight lines are $1/k_1[NO_2^+]$ and the slopes correspond to $k_{-1}/k_1k_2[NO_2^+]$.

In equations (7) and (8) the reaction rates have been expressed as functions of the reactant concentrations, although it is generally accepted that a better procedure is to employ activities.[8] The use of concentrations was dictated, of course, by the fact that activity coefficients for the species concerned in nitric acid solutions are not available. Any changes in activity coefficients with concentration will be reflected in variations of the values of the rate constants which are evaluated from the experiments.

To test the proposal that NO_2^+ is the active oxidant it is necessary to have the dependence of $[NO_2^+]$ upon the concentration variables. $[NO_2^+]$ is certainly very small in the region of interest for which the mole fraction of HNO_3 is in the range of 0·2–0·4. Therefore the possibility for evaluating the $[NO_2^+]$ dependence upon the HNO_3 concentration in aqueous solutions from information in the literature was investigated. The equilibria expected to be established are,

$$2\,HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O, \qquad K_1 \qquad (11)$$

and

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-. \qquad K_2 \qquad (12)$$

Reaction (12) effectively establishes the nitrate ion concentration. The activity of NO_2^+ is given by the expression,

$$a_{NO_2^+} = K_1 a_{HNO_3}[HNO_3]\gamma_{HNO_3}/a_{H_2O}[NO_3^-]\gamma_{NO_3^-}, \qquad (13)$$

where a's represent activities and γ's the molar activity coefficients. The activities of HNO_3 and H_2O in the solutions were obtained from the vapour pressure determination data for nitric acid solutions by TAYLOR[9] and the vapour pressure of pure nitric acid[10] and H_2O. RAO[11] reported the concentration of nitrate ions in nitric acid from 25° up to 90° from Raman spectrum intensities. Values of $[NO_3^-]/[HNO_3]$ have been estimated by an extrapolation of his reported degrees of dissociation to 100°C. This extrapolation introduced the major uncertainty because the degree of ionization depends rather strongly on temperature in this region. However, approxi-

[8] S. GLASSTONE, K. J. LAIDLER and H. EYRING, *The Theory of Rate Processes* p. 402. McGraw-Hill, New York (1941).
[9] G. B. TAYLOR, *Industr. Engng. Chem.* **17**, 633 (1925).
[10] E. P. EGAN, JR., *Industr. Engng. Chem.* **37**, 303 (1945).
[11] N. R. RAO, *Indian J. Phys.* **17**, 295 (1943).

mate values for the function in equation (14) could be evaluated. The expression in equation (14) is plotted in Fig. 2 versus the nitric acid normality.

$$a_{HNO_3}[HNO_3]/a_{H_2O}[NO_3^-] = a_{NO_2^+}\,\gamma_{NO_2^-}/K_1\gamma_{HNO_3} = K' a_{NO_2^+}. \qquad (14)$$

This function varies by a factor of about 40 over a range of concentrations of 12–16 N HNO_3. It was assumed that the variation of the function reflects primarily a change in the NO_2^+ activity because the activity coefficient ratio, $\gamma_{NO_2^-}/\gamma_{HNO_3}$, contained in K' is not expected to change by such an order of magnitude over this limited concentration range. γ_{HNO_3}, for example, was estimated from $a_{HNO_3}/[HNO_3]$ with the vapour pressure data and the degree of ionization function which were used for

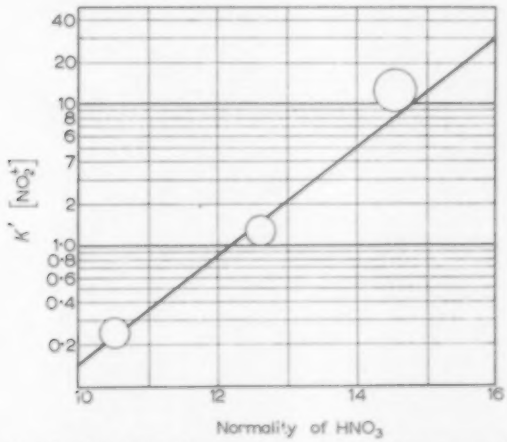

FIG. 2.—Estimated nitronium ion (NO_2^+) activity vs. the nitric acid concentration [equation (14)]. Each circle corresponds to an extrapolation of RAO's data.[11]

calculating the function in Fig. 2. Its variation was only a factor of about 2 from 11·7 N to 15·7 N HNO_3. In any event the uncertainty introduced by the use of the function in equation (14) appears to be no worse than the use of concentrations rather than activities in the rate expressions.

The NO_2^+ activity function for nitric acid solutions in Fig. 2 was used as an approximation for the corresponding property of cerium nitrate solutions. Indeed, because of the acidity of the cerium(III) and cerium(IV) it is not clear whether the NO_2^+ activity will be increased or decreased by the presence of the cerium nitrates.

For each kinetics experiment a plot of

$$K'[NO_2^+][Ce^{III}] \Big/ \frac{1}{V}\frac{dN_4}{dt} \text{ vs. } [Ce^{IV}]$$

was prepared.

Fig. 3 gives such plots for two of the experiments in which the HNO_3 concentration changed. It can be seen that approximately straight line functions were obtained despite such a variation in the nitric acid content. This feature was noted in general. According to equation (10) the intercepts of the straight lines equal (K'/k_1) and the slopes of the curves are $k_{-1}K'/k_1k_2$. The results of experiments at 100°C and for a gas flow of 131 l/hr are given in Table 1. In Table 2 are some results at 90°C and 110°C at some different flow rates.

From Table 1 it is seen that over a wide range of conditions the quantity k_1/K' was substantially constant. The relative standard deviation for all the values in Table 1 is 13 per cent, quite satisfactory in view of the experimental difficulties and uncertainties. However, the quantities k_{-1}/k_2 in Table 1 varied widely. In the proposed mechanism, which leads to equation (10), the reduction of HNO_3 was considered to

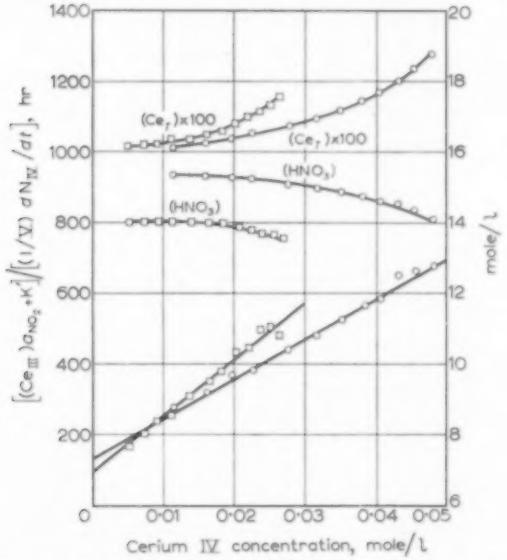

FIG. 3.—Rate dependence plots for two experiments with varying nitric acid concentration at 100°C and N_2 flow-rate of 131 l/hr.

TABLE 1.—INDICATED RATE CONSTANTS FOR THE OXIDATION OF Ce^{III} BY NITRIC ACID AT 100°C WITH A SWEEPING-GAS FLOW OF 131 l/HR

Initial Ce^{III} (mole/l.)	Nitric Acid (mole/l.)	1/intercept k_1/K' l/mole hr	Slope/intercept k_{-1}/k_2 (l/mole)
0·46	12·02 (constant)	0·0098	19
0·20	12·47 (constant)	0·0096	26
0·20	12·51 (constant)	0·0097	24
0·23	12·70 (constant)	0·0100	34
0·09	13·11 (constant)	0·0110	45
0·40	13·75 (constant)	0·0096	117
0·15	13·67 (constant)	0·0111	360
0·16	15·4–14·1	0·0076	86
0·20	15·1–14·1	0·0077	88
0·16	14·7–14·1	0·0083	106
0·15	14·4–13·8	0·0122	200
0·16	14·1–13·6	0·0105	170
0·16	14·0–13·6	0·0111	300

be effected only by the oxidation of cerium(III). The possibility exists that a spontaneous decomposition of nitric acid may lead also to the formation of NO_2. If this spontaneous decomposition proceeds at a constant rate, R, equation (7) is modified to give

$$(1/V)\, dN_{NO_2}/dt = k_1[Ce^{III}][NO_2^+] - k_{-1}[Ce^{IV}][NO_2] - k_2[NO_2] + R. \quad (15)$$

In place of equation (10), there is obtained,

$$\frac{[Ce^{III}][NO_2^+]}{\left(\frac{1}{V}\right)\left(\frac{dN_4}{dt}\right)} = \left(\frac{1}{k_1}\right)\left\{1 + \left(\frac{k_{-1}}{k_2}\right)[Ce^{IV}]\left(1 + \frac{R}{k_1[Ce^{III}][NO_2^+]}\right)\right.$$
$$\left. + \left(\frac{k_{-1}}{k_2}\right)^2[Ce^{IV}]^2\left(\frac{R}{k_1[Ce^{III}][NO_2^+]}\right)\left(1 + \frac{R}{k_1[Ce^{III}][NO_2^+]}\right) + \ldots\right\}. \quad (16)$$

Equation (16) predicts that a plot of $[Ce^{III}]K'[NO_2^+]/(1/V)(dN_4/dt)$ will be given by an infinite series in powers of $[Ce^{IV}]$ rather than by the straight line relation. It is noted, however, that the intercept of the function is just the same, i.e. K'/k_1, as in the case that no decomposition of nitric acid occurs. This intercept is also independent of the gas flow-rate. The slope of the function, even for small $[Ce^{IV}]$, depends upon the relative rates of the spontaneous decomposition and the oxidation reaction.

TABLE 2.—INDICATED RATE CONSTANTS FOR THE OXIDATION OF Ce^{III} BY NITRIC ACID AT 90° AND 110°C FOR DIFFERENT GAS FLOW-RATES

Temperature (°C)	Flow-rate (l/hr)	Initial Ce^{IV} (mole/l.)	Nitric acid (mole/l.)	1/intercept k_1/K' (l/mole hr)	Slope/intercept k_{-1}/k_2 (l/mole)
90	131	0·22	12·64 (constant)	0·005	80
90	162	0·21	12·44 (constant)	0·008	260
110	162	0·21	12·31 (constant)	0·0137	370
110	193	0·22	12·54 (constant)	0·0120	280

Since the decomposition of HNO_3 may well be a chain process it is not unreasonable for its rate to be sensitive to impurity traces, to surface effects or to light intensity which were not satisfactorily controlled. An increase in the flow-rate is expected to decrease the slope of the function, other factors remaining the same. This feature was observed in the experiments at 110°C in Table 2 but not at 90°C. However the very low rates at 90°C severely limit the accuracy of these values.

In summary, it appears that the kinetics data are consistent with an oxidation of Ce^{III} by NO_2^+ which is first order in each reactant. Yields of Ce^{IV}, far beyond the steady state concentrations in a static system, are attainable by the use of a sweeping-gas. However, rates of reaction are limited by the presence of NO_2 as the Ce^{IV}

concentration increases, even at the highest practical gas sweeping rates. At 100°C, it is believed that a significant decomposition of nitric acid occurs at an uncontrolled rate in the Ce^{III}–Ce^{IV} solutions. The temperature dependence of the constant, k_1/K', obtained from the intercepts corresponds to an Arrhenius activation energy of ca. 8 kcal. This quantity gives an estimated upper limit for the heat of formation of NO_2^+ from the nitric acid solutions.

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THE COPRECIPITATION OF RARE EARTHS WITH CALCIUM OXALATE

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Abstract—The mechanism of the uptake of rare earths by calcium oxalate has been studied in detail. ^{91}Y, ^{152}Eu and ^{154}Eu were used to obtain evidence of mixed crystal formation. It has been found that, out of the three hydrates of calcium oxalate claimed by earlier workers, it is calcium oxalate dihydrate which carries rare earths through mixed crystal formation. The uptake of rare earths by calcium oxalate monohydrate follows a Freundlich adsorption isotherm.

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IN a previous communication,[1] it was observed that calcium oxalate was a good carrier of rare earth and thorium activities. Mixed crystal formation of calcium fluoride with thorium and rare earth fluorides[2–4] has been well known. It is also reported[5] that calcium oxalate forms two definite hydrates other than the monohydrate which is the most stable form. It is of interest to study whether the carrying of rare earths by calcium oxalate shows evidence of mixed crystal formation. It is also of interest to see which of the hydrates forms mixed crystals with rare earth oxalates. Various methods[6,7] of radiochemical study of mixed crystal formation have been described. Of these, the technique adopted by KHLOPIN[4] on the study of the systems LaF_3–RaF_2, LaF_3–ThF_4 was found to be very convenient in one aspect. Another procedure adopted by us was the precipitation of the carrier by the slow release of precipitating ion through the hydrolysis of organic compounds,[8] which has recently been applied in radiochemistry. The direct addition of oxalate ion to precipitate calcium oxalate was also tried.

EXPERIMENTAL

Reagents used, such as calcium chloride, acetic acid etc., were all of Analar quality. The purity of ethyl oxalate, which was used in the slow precipitation technique to release oxalate ions through hydrolysis, was tested by determination of its boiling point. ^{91}Y and ^{152}Eu and ^{154}Eu used in the investigation were supplied by A.E.R.E., Harwell, England. The europium tracer was prepared by (n, γ) reaction upon natural europium.

In the series of experiments with preformed precipitate, calcium oxalate monohydrate was prepared in an acetic acid medium by precipitation with ammonium oxalate at about 80°C. This was filtered, washed free from other ions and dried at about 105° to constant weight. $CaC_2O_4 \cdot H_2O$ so obtained was powdered and filtered through 150 mesh. Different quantities of $CaC_2O_4 \cdot H_2O$ were taken in glass vessels of appropriate size stoppered with standard joints and containing a known volume of water to which was added a known amount of calcium chloride solution of known concentration. ^{91}Y, ^{152}Eu and ^{154}Eu tracers, as the case may be, with the appropriate amount of inactive element in

[1] B. C. PURKAYASTHA and S. N. BHATTACHARYYA, *J. Indian Chem. Soc.* **34**, 427 (1957).
[2] E. ZINTL and A. UDGÅRD, *Z. Anorg. Chem.* **240**, 150 (1939).
[3] J. A. A. KETELAAR and P. J. H. WILLEMS, *Rec. Trav. Chim.* **56**, 29 (1937).
[4] V. G. KHLOPIN and M. S. MERKULOVA, *Dokl. Akad. Nauk SSSR* **65**, 861 (1949); **71**, 689 (1950).
[5] V. KOHLSCHÜTTER and J. MARTI, *Helv. Chim. Acta* **13**, 929 (1930),
[6] O. HAHN, *Applied Radiochemistry*. Cornell University Press, New York (1936).
[7] A. C. WAHL and N. A. BONNER, *Radioactivity Applied to Chemistry*. John Wiley, New York (1951).
[8] L. GORDON, *Analyt. Chem.* **27**, 1704 (1955).

question as stated in the tables, were then added and the volume was made up to about 50 ml (about 3N acetic acid medium). The glass vessels were then placed in a thermostat (40 ± 0·05°C) and shaken by a mechanical shaker having about 70–80 vibrations per minute for several days (4 days) till equilibrium was attained. Radiochemical estimation of tracer was done as follows. The contents were separated and washed by centrifugation, and the activity of the solution and that of the precipitate were measured. Liquid counters were found to be very convenient for such a study.

The following procedure was adopted in the slow precipitation technique. Calcium chloride solution of known concentration, ethyl oxalate and some ethyl alcohol (40 per cent of the total volume) were taken in a series of glass tubes. The medium was made 3N with respect to acetic acid and about 1g ammonium acetate was added to neutralize the free mineral acid formed during the course of the reaction. ^{91}Y, ^{152}Eu and ^{154}Eu activity with appropriate inactive constituents were added. These were then placed in a thermostat (40 ± 0·05°) and shaken with a mechanical stirrer having about 70–80 vibrations per minute. The calcium oxalate formed was taken out at different intervals of time and the amounts precipitated were estimated. The activity remaining in solution was measured by a liquid counter and the homogeneous and heterogeneous distribution coefficients, D[9] and λ[10] were calculated from the following expressions.

$$D = \left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{Solid}} \Big/ \left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{Solution}} \tag{1}$$

$$\lambda = \log \frac{\text{Initial tracer}}{\text{Tracer in solution}} \Big/ \log \frac{\text{Initial carrier}}{\text{Carrier in solution}} \tag{2}$$

Another precipitation procedure was to add oxalic acid directly from a burette to calcium chloride solution, which was 3N with respect to acetic acid. Some amount of ammonium acetate was added to neutralize the free mineral acid generated during the course of the reaction. To avoid supersaturation, the solution was continuously stirred. Separation of the solid and the liquid phases was done by centrifugation. In the calculations, concentrations of tracer and carrier were taken as moles per litre.

DISCUSSION

In our studies with preformed $CaC_2O_4 \cdot H_2O$ precipitate we first of all determined the time required for the attainment of equilibrium. Instead of plotting the enrichment factor at different intervals of time we plotted the partition factor (D) (Fig. 1) which is more appropriate in this type of investigation. A glance at the figure will show that it required a minimum period of 4 days to erach equilibrium at 40°C.

Ratios of carrier to tracer were then changed to examine the constancy of the distribution factor. The distribution factors (D) were not, however, constant (Table 1). The data were in close agreement with a Freundlich adsorption isotherm (Fig. 2). We conclude that $CaC_2O_4 \cdot H_2O$ does not form mixed crystals with tracer amounts of rare earth oxalates.

Following earlier studies, we started precipitating calcium oxalate by oxalate ions released through slow hydrolysis of ethyl oxalate. It is interesting to note that Doerner–Hoskins' distribution law was nicely obeyed (Table 2). Such constancy of λ can only be accounted for by assuming that one of the hydrates other than the monohydrate carries rare earths through mixed crystal formation. It may further be noted that because of the fact that wider variations, as is evident from Table 2, was not possible in the system, we had to rely on the following evidence to show that this conclusion is quite genuine. Hydrolysis of ethyl oxalate was conducted at 98° and the products were separated as has already been described. λ was not found to be constant. The high temperature was selected to eliminate all hydrates other than the monohydrate. It was observed by earlier workers[5,11] that stability of the di- and

[9] L. M. HENDERSON and F. C. KRACEK, *J. Amer. Chem. Soc.* **49**, 738 (1927).
[10] H. A. DOERNER and M. HOSKINS, *J. Amer. Chem. Soc.* **47**, 662 (1925).

tri-hydrates decreases with rise of temperature and at high temperatures (~100°C) the stable phase that separates out is the monohydrate. The question naturally arises whether such a quick precipitation leads to any sound conclusion. The effect of speed of precipitation was studied by precipitating calcium oxalate from a solution

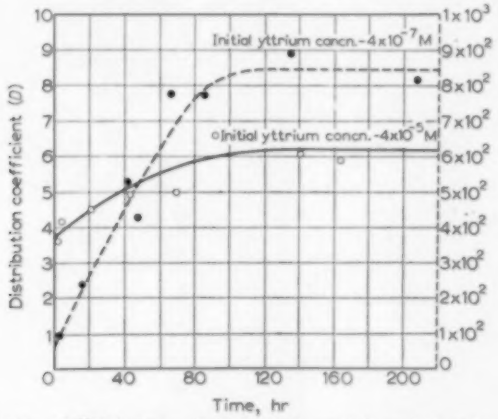

FIG. 1.—Distribution of ^{91}Y between $CaC_2O_4 \cdot H_2O$ crystals and its saturated solution in about 3N acetic acid medium at 40°C showing the attainment of equilibrium.
——— left hand side scale - - - - - right hand side scale

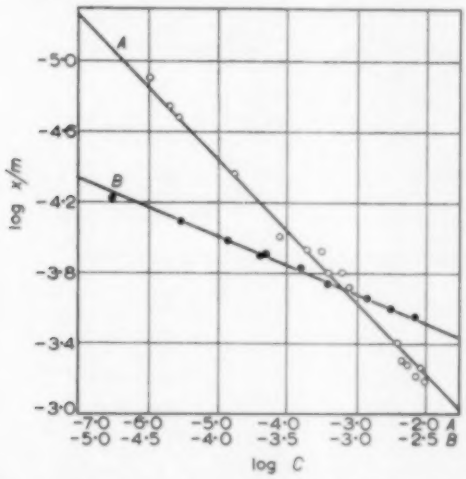

FIG. 2.—Freundlich adsorption isotherm on carrying of (*A*) europium and (*B*) yttrium by preformed $CaC_2O_4 \cdot H_2O$. *x*, amount of europium or yttrium carried (g/l.). *C*, concentration of europium or yttrium remaining in solution (g/l.), *m*, amount of $CaC_2O_4.H_2O$ (g/l.).

of calcium chloride in acetic acid by adding oxalic acid from a burette at 32°C. The rate of precipitation in this case was in no way slower than the precipitation made by hydrolysis of ethyl oxalate at the higher temperatures already mentioned. We found that the λ values were constant (Table 3). But this constancy is not, however, observed if we go on increasing the period of contact between solid and liquid phases under constant stirring before separation. Even if we separate after 1 hr (Table 3) the values of λ tend to decrease with increasing quantity of carrier precipitated. With longer

[11] E. B. SANDELL and I. M. KOLTHOFF, *J. Phys. Chem.* **37**, 153 (1933).

TABLE 1.—THE DISTRIBUTION OF ^{91}Y, ^{152}Eu AND ^{154}Eu BETWEEN PREFORMED $CaC_2O_4 \cdot H_2O$ CRYSTALS AND ITS SATURATED SOLUTION IN ABOUT 3 N ACETIC ACID MEDIUM AT 40°C

Calcium in solid phase (%)	Tracer (^{91}Y, ^{152}Eu and ^{154}Eu in solid phase)(%)	D
(a) Initial yttrium concentration—4×10^{-5} M		
5·9	25·8	5·55
12·1	50·6	7·44
17·5	66·8	9·49
23·3	81·9	14·89
28·4	88·8	19·99
34·1	94·0	30·27
(b) Initial yttrium concentration—4×10^{-6} M		
2·5	46·7	34·2
4·2	67·2	46·7
6·6	84·3	76·0
9·7	95·1	180·7
(c) Initial europium concentration—$9·09 \times 10^{-7}$ M		
2·64	87·3	253
5·77	97·9	761
6·90	98·6	950
9·60	99·2	1168
(d) Initial europium concentration—$8·79 \times 10^{-6}$ M		
2·8	42·6	25·8
4·1	53·5	26·9
5·2	69·7	41·9
7·4	75·7	39·0
8·5	86·2	67·2
10·9	94·1	130·4
(e) Initial europium concentration—$7·97 \times 10^{-5}$ M		
3·4	20·3	7·24
5·3	26·3	6·37
7·0	40·4	9·01
10·6	55·3	10·43
13·3	65·0	12·11
16·6	69·0	11·18

N.B. Amount of calcium taken was 715 mg in 50 ml in the case of (a) and (b); the same amount of calcium (715 mg) was present in 25 ml in the case of (c), (d) and (e).

TABLE 2.—THE CO-PRECIPITATION OF RARE EARTHS WITH CALCIUM OXALATE PRECIPITATED BY THE SLOW HYDROLYSIS OF ETHYL OXALATE IN ACETIC ACID MEDIUM AT 40°C

Reaction time (hr)	Calcium precipitated (%)	Tracer (^{91}Y, ^{152}Eu and ^{154}Eu precipitated) (%)	λ	λ_p	D
(A) Initial yttrium concentration—$1{\cdot}5 \times 10^{-6}$ M					
7	0·80	56·1	102·1	—	158
—	0·88	57·2	97·0	89·3	—
—	0·94	60·1	97·3	—	159
—	1·26	69·9	94·8	93·0	—
8	1·34	70·0	90·2	—	172
9	1·52	77·9	99·3	—	228
10	1·88	86·0	104·1	—	321
		Average	97·8		
(B) Initial yttrium concentration—$2{\cdot}7 \times 10^{-7}$ M					
8	0·91	59·7	98·7	—	161
9	1·31	72·8	99·2	—	202
10·5	2·11	87·4	96·7	—	322
		Average	98·2		
(C) Initial yttrium concentration—4×10^{-6} M					
12	1·05	60·7	88·2	—	145
12·75	1·82	80·4	89·6	84·5	221
14·25	2·80	91·8	88·3	—	389
15	2·94	92·4	86·7	—	401
		Average	88·2		
(D) Initial europium concentration—$2{\cdot}4 \times 10^{-6}$ M					
12	1·33	73·8	100·3	—	209
13	1·68	81·8	101·4	—	263
14	2·31	90·0	98·0	97·0	381
15	3·22	95·3	93·5	—	609
15·8	3·78	97·4	94·9	—	954
		Average	97·6		

N.B. (A) and (B)—In both these series of experiments the initial amount of calcium taken was 908 mg in 75 ml, and the amount of ethyl oxalate taken was 5·4 g i.e., 1·63 times the stoicheiometric quantity required for complete precipitation of calcium.
(C) and (D)—In these sets of experiments the calcium taken initially was 1430 mg in 50 ml, and the amount of ethyl oxalate taken was 5·4 g, which is 1·03 times the stoicheiometric quantity required for complete precipitation of calcium.
λ_p indicates some values of λ computed from activities measured from the precipitate. λ and D represent the respective values calculated from the activity of the solution left after separation.

TABLE 3.—THE CARRYING OF RARE EARTHS BY CALCIUM OXALATE PRECIPITATED BY THE ADDITION OF OXALIC ACID TO A SOLUTION OF CALCIUM CHLORIDE IN ACETIC ACID MEDIUM AT 32°C

	Calcium precipitated (%)	Europium (^{153}Eu and ^{154}Eu) precipitated (%)		λ	D
(a)	1·55	27·6		20·6	24·2
	2·43	36·5		18·4	23·1
	5·02	67·6		21·9	39·5
	7·97	78·5		18·5	42·2
			Average	19·8	
(b)	2·80	43·9		20·4	27·2
	6·15	76·0		22·5	48·3
	10·21	84·8		17·5	48·1
			Average	20·1	
(c)	0·91	18·3		21·9	24·4
	2·85	45·3		20·8	28·2
	5·24	73·5		24·6	50·2
	6·85	80·5		23·0	56·1
	8·52	85·4		21·6	62·8
	10·71	88·7		19·2	65·4
			Average	21·8	
(d)	1·89	40·4		27·1	35·2
	5·17	75·1		26·1	55·3
	8·74	89·9		25·1	93·0
(e)*	0·45	28·8		73·7	89·5
	0·88	40·6		59·5	77·0
	1·21	40·8		43·0	56·3
	2·21	50·0		31·0	44·2
	4·29	71·6		28·6	56·2
	5·89	77·1		24·2	53·8

Initial europium concentration $9{\cdot}09 \times 10^{-7}$ M
Initial calcium concentration $7{\cdot}15 \times 10^{-1}$ M

N.B. Calcium oxalate formed after requisite addition of oxalic acid was stirred at a constant rate for different intervals of time.
(a) No stirring but rapid separation of the solid and solution by centrifugation:
(b), (c), (d) and (e) Stirring for 2, 10, 60 min and 24 hr respectively.
* Data were taken at 35°C. Initial calcium concentration taken here was $8{\cdot}72 \times 10^{-1}$ M.

periods the values of λ vary widely. This result may be due to the breaking down of the unstable higher hydrate, which is initially formed during the course of precipitation. In our experiments with preformed $CaC_2O_3 \cdot H_2O$ it was further observed by us that even 0·1 mg of inactive yttrium was sufficient to damp down the adsorption capacity to a very large extent (Fig. 1). But in our study with slow hydrolysis under the same concentration limits the λ values are about the same (Table 2). A slightly lower value may be attributed to the complex oxalato ion formation at finite concentration.[12,13] Therefore one of the hydrates other than the monohydrate is responsible for carrying rare earths through mixed crystal formation. There are three hydrates (mono-, di- and tri-) of calcium oxalate.[5] The di- and the tri- hydrates are the transient phases which predominate respectively in acidic and ammoniacal mediums.[5] Our study in a slightly ammoniacal medium (Table 4) reveals that neither D nor λ is constant,

TABLE 4*.—THE CARRYING OF RARE EARTHS BY CALCIUM OXALATE PRECIPITATED BY THE ADDITION OF AMMONIUM OXALATE TO A SOLUTION OF CALCIUM CHLORIDE IN SLIGHTLY AMMONIACAL MEDIUM AT 35°C

Calcium precipitated (%)	Tracer (^{152}Eu and ^{154}Eu) precipitated (%)	λ	D
0·62	53·4	118·4	183·6
1·66	67·8	68·4	124·7
2·93	74·8	46·1	98·3
4·36	77·0	33·1	73·4
6·04	77·5	24·0	53·6

Initial europium concentration $4{\cdot}54 \times 10^{-7}$ M
Initial calcium concentration $4{\cdot}36 \times 10^{-1}$ M

* Calcium oxalate formed after requisite addition of ammonium oxalate was immediately separated through centrifugation.

but the extent of carrying is about the same order as that found in an acidic medium. From these results in an ammoniacal medium it is thus evident that the calcium oxalate trihydrate which is said to be the predominating phase[5] does not form mixed crystals with rare earth oxalates. The constancy of λ in acidic conditions is then clear evidence that $CaC_2O_4 \cdot 2H_2O$ (which has been observed to be the predominating phase[5]) forms mixed crystals with rare earth oxalates. The dihydrate is not however a stable phase. The decomposition of the dihydrate to monohydrate is clearly indicated from our result that we do not get either D or λ constant if the calcium oxalate thus precipitated is separated after a longer period.

It is of interest to note that the study of the distribution laws (Berthelot–Nernst and Doerner–Hoskins) is of much importance in revealing the existence of unstable phases in the process of precipitation. Radioactive isotopes now available are a great aid in such studies.

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[12] P. B. SARKAR, *Bull. Soc. Chim.* **41**, 185 (1927).
[13] J. STERBA-BOHM and A. PISARICEK, *Coll. Czech. Chem. Comm.* **2**, 244 (1930).

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THE CHEMISTRY OF URANYL NITRATE–HYDROXIDE–UREA SYSTEMS*

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Abstract—The reaction mechanism has been determined for addition of ammonium hydroxide or sodium hydroxide to a solution of uranyl nitrate and urea. Evidence has been presented to show that nitrouranic acid [$UO_2(NO_3)OH$] and hydrated uranic acid ($H_2UO_4 \cdot H_2O$) are intermediate compounds. Finally, a discussion of the relationship of these intermediates to the chemistry of uranates is presented.

IN THE course of some experiments conducted in these laboratories, the necessity arose for the recovery of uranium from solutions containing large quantities of urea. Ammonium hydroxide was added to the system in order to precipitate "ammonium diuranate". The physical properties of the product obtained suggested that a chemical species other than the "diuranate" was present whereas washing the product with water affected its chemical nature as was indicated by variations in the analytical data. A systematic investigation was therefore undertaken to elucidate further the chemistry of the reaction.

EXPERIMENTAL

Materials

Uranyl nitrate hexahydrate (Baker and Adamson, A.C.S.) and the urea (American Cyanamid Company) were used without further purification.

Analysis

Urea was determined according to a procedure described by GERTNER and INKOVIK.[1] Nitrogen was determined by the Kjeldahl method and uranium was assayed by ignition to urano-uranic oxide (U_3O_8).

(1) *Urea uranate.* A precipitate resulting from the addition of 24 ml of concentrated ammonium hydroxide to 100 ml of an 8 M solution of urea containing 400 g/l. uranium was washed with methyl alcohol and air-dried. X-ray diffraction data for this yellow compound, urea uranate, are shown in Table 1. (Found: U, 55·93; urea, 28·21; N, 13·11. Calc. for $H_2UO_4 \cdot 2CO(NH_2)_2$: U, 56·12; urea, 28·32; N, 13·21%).

(2) *Urea nitrouranate.* (a) One hundred millilitres of an 8 M urea solution containing 400 g/l. uranium gave upon addition of 5·36 g of sodium hydroxide, a product which was then washed with alcohol. (Found: U, 58·44; urea, 14·85; N, 10·15. Calc. for $UO_2(OH)NO_3 \cdot CO(NH_2)_2$: U, 58·19; urea, 14·67; N, 10·26%).

(b) Addition of 13·4 ml of concentrated ammonium hydroxide to 150 ml of an 8 M urea solution containing 400 g/l. uranium yielded a bright yellow precipitate which was washed with methyl alcohol. (Found: U, 58·48; urea, 15·00; N, 10·36. Calc. for $UO_2(OH)NO_3 \cdot CO(NH_2)_2$: U, 58·19; urea 14·67; N, 10·26%).

Thus, an identical product, urea nitrouranate, is obtained upon addition of NH_4OH or NaOH to uranyl nitrate–urea solutions.

* This paper is based on work performed for the Atomic Energy Commission by the National Lead Company of Ohio at Cincinnati, Ohio.

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[1] A. GERTNER and H. INKOVIK, *Z. Anal. Chem.* **142**, 36 (1954).

(3) *Nitrouranic acid.* Urea nitrouranate was refluxed with water for 4 hr in a Soxhlet extractor. The residue was air-dried prior to analysis. (Found: U, 68·21; N, 4·10. Calc. for $UO_2(OH)NO_3$: U, 68·19; N, 4·01%).

Urea nitrouranate and nitrouranic acid yielded X-ray diffraction patterns indicating amorphous structures.

(4) *Hydrated uranic acid.* (a) Freshly precipitated urea uranate was refluxed with water in a soxhlet extractor for 4 hr. Chemical analysis of the residue corresponded to hydrated uranic acid, $H_2UO_4 \cdot H_2O$. (Found: U, 73·86. Calc. for $H_2UO_4 \cdot H_2O$: U, 73·91%).

(b) To 250 ml of a 400 g/l. uranium solution was added 27·3 ml of concentrated ammonium hydroxide. The product was washed, air-dried and analysed. (Found: U, 73·79. Calc. for $H_2UO_4 \cdot H_2O$: U, 73·91%).

(c) In a similar manner, a concentrated solution of sodium hydroxide (16·8 g/50 ml) was added to 250 ml of a 400 g/l. uranium solution yielding a yellow precipitate. (Found: U, 73·85. Calc. for $H_2UO_4 \cdot H_2O$: U, 73·91%).

The X-ray diffraction patterns from 4(a), (b) and (c) were identical and corresponded to the "hydrate" $UO_3 \cdot 2H_2O$ reported by DAWSON *et al.*[2]

TABLE 1.—X-RAY DIFFRACTION DATA FOR UREA URANATE

d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
7·76	100	3·91	10	3·30	50d
7·35	10d	3·79	15	3·19	10d
6·03	15	3·65	15	3·14	10d
5·08	40	3·52	10*d*	2·97	15

d = diffuse.

DISCUSSION

Supporting evidence for the formation of hydrated uranium trioxide as the initial product upon addition of base to uranyl nitrate solutions was obtained by TRIDOT,[3] using pH and conductimetric techniques, BRITTON,[4,5] on the basis of electrometric measurements, and by RICCI and LOPREST,[6] as shown in equilibrium mixtures by phase-rule studies. WAMSER *et al.*[7] in their study of uranate systems concluded that addition of 2·29 moles of NaOH/mole uranium yields $Na_2U_7O_{22}$ as the initial product, whereas, FLATT and HESS[8] asserted from phase-rule studies, that a uranate is initially formed.

From the data obtained in this investigation, isolation of $H_2UO_4 \cdot H_2O$ under various conditions substantially confirmed the findings of TRIDOT, BRITTON, and RICCI. However, their interpretation of this compound as a hydrated oxide would be inadequate to account for its conversion to urea uranate which can best be explained by the presence of acidic groups. It is interesting to note that this acid, which forms a series of acids,[9] was shown by X-ray diffraction data to be identical with the "hydrate", $UO_3 \cdot 2H_2O$, described by DAWSON *et al.*[2]

[2] J. K. DAWSON, E. WAIT, K. ALCOCK and D. R. CHILTON, *J. Chem. Soc.* 3531 (1956).
[3] G. TRIDOT, *Ann. Chem.* **5**, 358 (1950).
[4] H. T. S. BRITTON, *J. Chem. Soc.* 2148 (1925).
[5] H. T. S. BRITTON and J. YOUNG, *J. Chem. Soc.* 2467 (1932).
[6] J. E. RICCI and F. LOPREST, *J. Amer. Chem. Soc.* **77**, 2119 (1955).
[7] C. A. WAMSER, J. BELLE, E. BERNSOHN and B. WILLIAMSON, *J. Amer. Chem. Soc.* **74**, 1020 (1952).
[8] R. FLATT and W. HESS, *Helv. Chim. Acta.* **21**, 1506 (1938).
[9] P. S. GENTILE, L. H. TALLEY and T. J. COLLOPY, *J. Inorg. Nucl. Chem.* **10**, 114 (1959).

Sufficient evidence was also obtained to make it reasonable to assume that for a uranyl nitrate-hydroxide-urea system, the following mechanism could be proposed:

$$UO_2(NO_3)_2 + NH_4OH \longrightarrow UO_2(OH)NO_3 + NH_4NO_3 \quad (1)$$

$$UO_2(OH)NO_3 + CO(NH_2)_2 \longrightarrow UO_2(OH)NO_3 \cdot CO(NH_2)_2 \quad (2)$$

$$UO_2(OH)NO_3 \cdot CO(NH_2)_2 + NH_4OH \longrightarrow H_2UO_4 \cdot CO(NH_2)_2 + NH_4NO_3 \quad (3)$$

$$H_2UO_4 \cdot CO(NH_2)_2 + CO(NH_2)_2 \longrightarrow H_2UO_4 \cdot 2CO(NH_2)_2 \quad (4)$$

Equations (2) and (4) were confirmed by the isolation of urea nitrouranate and urea uranate, which upon refluxing with water, yielded the respective acids. The existence of UO_2OH^+ as an intermediate species [equation (1)] seems reasonable and has previously been postulated by other investigators.[10,11] The failure to precipitate nitrouranic acid upon addition of base to uranyl nitrate solutions indicated that $UO_2(OH)NO_3$ is present in solution and the addition of a reagent such as urea is required for precipitation and isolation. The product $H_2UO_4 \cdot CO(NH_2)_2$ illustrated in equation (3) could not be isolated though its temporary formation seems reasonable. WAMSER's observation that weak bases such as pyridine and aniline react with uranyl salts to precipitate $UO_3 \cdot H_2O$ could not be duplicated. In contrast, BARR and HORTON's work[12] led to insoluble complex formation with pyridine, whereas, the reaction with urea, thiourea and guanidine have been shown[13,14] to yield soluble co-ordination compounds.

The most significant application of the interpretation of $UO_3 \cdot H_2O$ as the dibasic acid, H_2UO_4, is found in proposing that this reagent reacts with bases to form hydrogen uranates and uranate salts which reasonable explains the diversity of uranates previously reported. SUTTON[15] recently favoured the formation of $Na_2U_{16}O_{49}$ (yellow) and the "true" diuranate, $Na_2U_2O_7$ (oranage) while WAMSER *et al.*[7] concluded that two uranates $Na_2U_7O_{22}$ (yellow) and $Na_6U_7O_{24}$ (orange) are formed. FLATT and HESS[8] found two uranates $K_2U_7O_{22} \cdot xH_2O$ (yellow) and $K_4U_5O_{17} \cdot xH_2O$ (orange) but their failure to observe the diuranate $K_2U_2O_7$ even in strongly alkaline solutions led them to believe that this compound is not obtainable by aqueous methods.

The uranates described by previous investigators can, in general, be divided into three groups, namely uranates, hydrogen uranates and polyuranates containing alkali metal/U mole ratios of 2 : 1 (Na_2UO_4), approximately 1 : 1 ($Na_6U_7O_{24}$,$Na_2U_2O_7$, $K_4U_5O_{17}$) and 1 to 3 or 4 ($K_2U_7O_{22} \cdot xH_2O$, $Na_2U_8O_{25}$, $Na_2U_5O_{16}$, $Na_2U_7O_{22}$).

The compound $CaUO_4$ isolated by TANFORD[11] and Na_2UO_4 obtained by TRIDOT[3] from excessively basic solutions are probably true uranates. Those compounds having an alkali metal/U ratio of approximately 1 : 1 are probably hydrogen uranates (i.e. $NaHUO_4$). The titration techniques used by previous investigators are insufficient for distinguishing diuranates (or pyrouranates) from hydrogen uranates and the present data provides stronger support for the latter. Moreover, diuranates

[10] R. J. BEST, D. TAUB and L. G. LONGWORTH, Report A-380, November 24, 1942.
[11] C. TANFORD, R. L. TECHENOR and H. A. YOUNG, *J. Amer. Chem. Soc.* **73**, 4491 (1951).
[12] J. T. BARR and C. A. HORTON, *J. Amer. Chem. Soc.* **74**, 4430 (1952).
[13] P. S. GENTILE and L. H. TALLEY, *J. Amer. Chem. Soc.* **79**, 4296 (1957).
[14] P. S. GENTILE and L. H. TALLEY, *J. Amer. Chem. Soc.* **79**, 5889 (1957)
[15] J. SUTTON, *J. Inorg. Nucl. Chem.* **1**, 68 (1955).

have mainly been prepared by high temperature reactions.[16,17,18] Finally, the ease of hydrolysis of pyrouranic acid ($H_2U_2O_7$) to uranic acid was shown[9] to be indicative of the instability of diuranates in aqueous media.

For the last group of compounds, with ratios of 1 to 3 or 4, it seems reasonable to assume that they are mixtures of uranic acid and hydrogen uranates obtained by hydrolysis of uranates and hydrogen uranates or by the addition of insufficient base. The deleterious effects of washing residues from uranate systems have been cited previously.[6,7,19]

In view of the evidence presented, the formation of a diuranate instead of a uranate in an aqueous uranate system is questionable. Further study is necessary utilizing techniques which can distinguish diuranates from hydrogen uranates to conclusively resolve this problem.

Acknowledgement—We are indebted to H. A. HELLER for the X-ray data and their interpretation, and to B. GESSINESS and his staff for the analytical results.

[16] H. R. HOEKSTRA and J. J. KATZ, *J. Amer. Chem. Soc.* **74**, 1683 (1952).
[17] C. ZIMMERMANN, *Liebigs Ann.* **213**, 285 (1882).
[18] R. BERSOHN and E. L. BRADY, *U.S.A.E.C. Mon. C.* 109 (1946).
[19] J. METZGER and M. HEIDELBERGER, *J. Amer. Chem. Soc.* **31**, 1040 (1909).

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SOME EVIDENCE FOR THE PRESENCE OF URANIC ACID IN URANIUM TRIOXIDE–WATER SYSTEMS*

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(*Received* 17 *October* 1958)

Abstract—The hydrates, $UO_3 \cdot 2H_2O$, $UO_3 \cdot 0{\cdot}8H_2O$ and $UO_3 \cdot 0{\cdot}5H_2O$ described by DAWSON *et al.*[1] were shown to react with the organic base, urea, to form urea uranate $H_2UO_4 \cdot 2CO(NH_2)_2$. The formation of this salt provides evidence that these "hydrates" constitute a series of acids whose relationship may be expressed as follows: $H_2UO_4 \cdot H_2O \xrightarrow{100°C} H_2UO_4 \xrightarrow{160°C} H_2U_2O_7$ (pyrouranic acid). Attempts to characterize the "hydrate" $UO_3 \cdot 0{\cdot}8H_2O$ were unsuccessful; instead the presence of a mixture of H_2UO_4 and $H_2U_2O_7$ was indicated.

IN a recent communication, DAWSON *et al.*[1] described some aspects of a uranium trioxide–water system and the hydrates formed. In connexion with work conducted in these laboratories, it became necessary to further study these reactions to determine whether hydrates or acids are formed since evidence[2] was presented for the existence or uranic acid in uranyl nitrate–ammonia–urea systems.

EXPERIMENTAL

The UO_3 was prepared by thermal denitration of uranyl nitrate hexahydrate while all other chemicals employed were reagent grade. X-ray diffraction patterns were obtained with a Norelco X-ray diffraction unit; the analytical procedures are described elsewhere.[2]

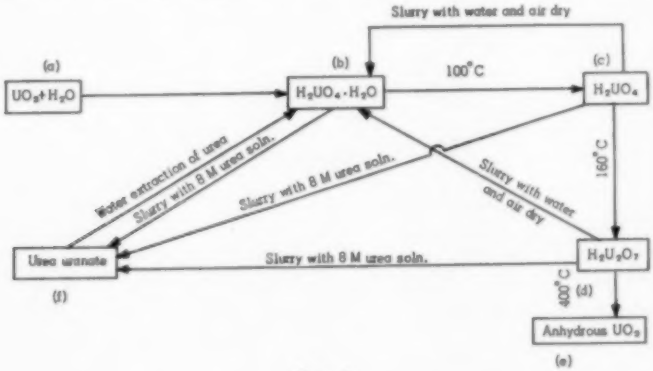

FIG. 1.

Uranium trioxide§ (a) was slurried in water at room temperature and the resulting product (b) $H_2UO_4 \cdot H_2O$ was filtered and air-dried. After dehydration of (b) at 100°C for 1 hr, the compound

* This paper is based on work performed for the Atomic Energy Commission by National Lead Company of Ohio, Cincinnati, Ohio.

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§ Type III[3] uranium trioxide produced through thermal denitration from aqueous uranyl nitrate by the National Lead Company of Ohio.

[1] J. K. DAWSON, E. WAIT, K. ALCOCK and D. R. CHILTON, *J. Chem. Soc.* 3531 (1956).

[2] P. S. GENTILE, L. H. TALLEY and T. J. COLLOPY, *J. Inorg. Nucl. Chem.* **10**, 110 (1959).

[3] H. R. HOEKSTRA and S. SIEGEL, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/1548.

(c) H_2UO_4 was obtained, which upon subsequent heating at 160°C for 3 hr, yielded (d) $H_2U_2O_7$ (pyrouranic acid). A cycle was completed when water slurries of (c) and (d) gave products identical to (b). Anhydrous UO_3 (e) was produced by heating (d) at 400°C for 1 hr. It was further shown that the salt (f), urea uranate, could be obtained by slurrying 10 g samples of (b), (c) or (d) in 250 ml of an 8 M solution of urea and then washing the product with methyl alcohol. Typical analytical data for these compounds are shown in Table 1.

TABLE 1

Compound	U (%) calc.	U (%) found	Urea (%) calc.	Urea (%) found
(a) UO_3	83·22	83·09	—	—
(b) $H_2UO_4 \cdot H_2O$	73·91	73·85	—	—
(c) H_2UO_4	78·29	78·21	—	—
(d) $H_2U_2O_7$	80·68	80·74	—	—
(e) Anhydrous UO_3	83·22	83·11	—	—
(f) $H_2UO_4 \cdot 2CO(NH_2)_2$	56·12	55·93	28·32	28·21

X-ray data of (b) $H_2UO_4 \cdot H_2O$, (c) H_2UO_4, and (d) $H_2U_2O_7$ demonstrated that these compounds were identical with Dawsons's $UO_3 \cdot 2H_2O$, $UO_3 \cdot 0{\cdot}8H_2O$ and $UO_3 \cdot 0{\cdot}5H_2O$ hydrates, respectively. In every case, chemical analysis and X-ray diffraction patterns were obtained in order to confirm the relationship between the compounds as illustrated in Fig. 1. The diffraction pattern of urea uranate was identical with data previously reported.[2]

DISCUSSION

From the chemical evidence obtained, it seems reasonable to assume that the "hydrates" constitute a series of acids since their conversion to urea uranate can best be explained by the presence of acidic groups in these compounds.*

It would then follow that uranic acid monohydrate should loose one molecule of water at a relatively low temperature. This was demonstrated by its conversion to uranic acid below 100°C. The further loss of 0·5 mole of water at a relatively higher temperature (160°C) and the retention of the last 0·5 mole of water below 400°C, only becomes reasonable if the formation of pyrouranic acid is assumed in preference to a "hemihydrate."

Attempts to characterize the "hydrate" $U_3O_8 \cdot 0{\cdot}8H_2O$ were unsuccessful, instead, the presence of a mixture was indicated. Since partial dehydration of H_2UO_4 results in a mixture of H_2UO_4 and essentially amorphous $H_2U_2O_7$, it would be anticipated that the X-ray diffraction pattern of such a mixture would not be appreciably different from H_2UO_4 alone. This reasoning is supported by the similarity of interplanar spacings for H_2UO_4 and $UO_3 \cdot 0{\cdot}8H_2O$. In addition, conversion of H_2UO_4 to $H_2U_2O_7$ at 160°C contradicts the wide temperature range (150°–250°C) reported by DAWSON for the stability of the "hydrate" $UO_3 \cdot 0{\cdot}8H_2O$.

Evidence in the literature for other "hydrate" compounds of uranium trioxide suggest that polymorphic forms of uranic acid may exist although they could be hydrates. These questions are being resolved through further study.

* We are indebted to Dr. R. H. MOORE, General Electric Company, Hanford, Washington, for revealing unpublished infra-red data which are in substantial agreement with our findings.

One further point of interest may be found in the ease of hydrolysis of (d) pyrouranic acid to (b) uranic acid monohydrate in aqueous media at room temperature. Its significance becomes evident in the study of uranate systems by providing supporting evidence for FLATT and HESS[4] contention that diuranate (or pyrouranates) cannot be prepared in aqueous media.

Acknowledgement—We are indebted to H. A. HELLER of the Analytical Department of National Lead Company of Ohio for the X-ray data and their interpretation.

[4] R. FLATT and W. HESS, *Helv. Chim. Acta* **21**, 1506 (1938).

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ISOLATION OF NEPTUNIUM AS A MONO OCTYL PHOSPHORIC ACID COMPLEX BY LIQUID–LIQUID EXTRACTION*

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Abstract—The extraction of certain M(III), M(IV) and M(VI) actinides and lanthanides and Y(III) in the system mono(2-ethylhexyl) orthophosphoric acid (symbolized as H_2MEHP) in toluene diluent vs. aqueous HCl has been investigated with respect to operational solvent and acid dependencies, state of oxidation, and Z, using the radioactive tracer technique. Through proper combination of solvent concentration and HCl concentration, systems may be devised by means of which M(IV) may be separated from M(VI) and M(III), or M(VI) may be separated from M(III).

The ratio of the K values for Np(IV) and Np(VI) respectively exceeds 10^5 as does the ratio of the respective K values for U(IV) and U(VI). The ratio of the K value of Np(IV) to the K values of U(VI) and Pu(III) may be made greater than 10^4.

A flow sheet for the isolation of Np as Np(IV) has been devised and tested. This procedure requires only a single extraction with H_2MEHP (in toluene) followed by multiple scrubbing with 12 F HCl containing hydroquinone, or 6 F HCl containing hydroquinone and hydriodic acid, the reducing agents serving to reduce plutonium to Pu(III).

The mechanism of extraction has been examined tentatively in terms of ion exchange analogy and chloride complexing. The anti-synergistic interaction of TBP (tri-*n*-butyl phosphate) with H_2MEHP has been utilized in effecting the return of Np(IV) to an aqueous phase.

IT is widely recognized that in general the tendency for a given element to extract from an aqueous phase into an equilibrated opposing organic phase is not only a function of atomic number but is also strongly dependent upon the state of oxidation of the element. As a corollary, it is to be expected that the mutual separation of a pair of chemically similar elements by liquid–liquid extraction will be realized more easily in systems in which the two elements exist in mutually different valence states than in systems in which they exist in the same valence state.

Since the 4+ and 6+ oxidation states of neptunium are easily realizable in aqueous solution, the separation of neptunium from fission product lanthanides in their 3+ states by liquid–liquid extraction, ion exchange, and carrier techniques has been accomplished readily. Likewise, the separation of Np(IV) from U(VI) has proved to be a comparatively simple problem.

However, under the specification of high mutual decontamination, the neptunium–plutonium partition is a difficult one. This difficulty arises from the fact that of all the possible combinations of valence states in which neptunium and plutonium differ, Pu existing in aqueous solution as Pu(III), Pu(IV) and Pu(VI), only the combination of Np(IV) and Pu(III) is readily realizable in a given solution under conditions of multiple extraction and multiple scrubbing.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission and reported, in large part, at the Third Annual Meeting of the American Nuclear Society, Pittsburgh, Pennsylvania, U.S.A. (1957).

Consequently, assuming that a system exists in which the organic solvent differentiates strongly in favour of Np(IV) as opposed to Pu(III), the over-all problem of separating ^{237}Np, from any material (excluding Zr and Nb) resulting from the processing of neutron-irradiated uranium, in high yield and high purity, is reduced, in its essentials, to the two problems of transferring the neptunium as Np(IV) in high yield to a suitable solvent and of reducing plutonium to Pu(III).

A solvent consisting of mono(2-ethyl hexyl) ortho phosphoric acid, symbolized as H_2MEHP, dissolved in a carrier solvent such as toluene has been found to extract Np(IV) in high yield from an aqueous HCl phase under conditions favouring the rapid reduction of Pu(IV) to the poorly extracting Pu(III). A flow sheet for the separation of ^{237}Np from U, Pu, Am, Cm, and fission product lanthanides and Y based on these observations has been devised.

EXPERIMENTAL

Sources of materials

A mixture of the mono- and dioctyl orthophosphoric acids (2-ethyl hexyl isomer), consisting primarily of these acids, was obtained from Victor Chemical Works. The mono (2-ethyl hexyl) phosphoric acid, symbolized as H_2MEHP, was separated and purified as reported by PEPPARD *et al.*[1] The tri-*n*-butyl orthophosphate, symbolized as TBP, was obtained from Commercial Solvents Corporation and purified as reported by PEPPARD *et al.*[2]

The β-active nuclides 40·2 hr ^{140}La (with parent 12·8 day ^{140}Ba), 285 day ^{144}Ce, 2·6 year ^{147}Pm, 13 year ^{155}Eu and 16 year ^{154}Eu, 58 day ^{91}Y, 65 day ^{95}Zr and 45 day ^{181}Hf were obtained from the Isotopes Division of the Oak Ridge National Laboratory. β-Active 2·33 day ^{239}Np was obtained from J. C. HINDMAN of this laboratory. The α-active nuclides $8{\cdot}0 \times 10^4$ year ^{230}Th, $1{\cdot}6 \times 10^5$ year ^{233}U, $2{\cdot}2 \times 10^6$ year ^{237}Np, $2{\cdot}43 \times 10^4$ year ^{239}Pu, and 470 year ^{241}Am were obtained from A.N.L. stocks. α-Active 18 year ^{244}Cm was obtained from P. R. FIELDS of this laboratory. All of the foregoing tracers were subjected to further purification cycles using liquid–liquid extraction techniques.

Determination of distribution ratio

The distribution ratio, K, of a specific nuclide, here defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two equilibrated sensibly immiscible liquid phases was determined radiometrically as previously reported,[1] with the exceptions noted. All distribution ratio values are for experiments involving 3 min mixing periods.

In general, the K for a specific set of conditions for a given nuclide has been determined both in a "direct" extraction and a "reverse" extraction. The nuclide is extracted from an aqueous phase into an initially barren pre-equilibrated organic phase (direct extraction). Following the withdrawal of samples for analysis, the pregnant organic phase is then contacted with an initially barren pre-equilibrated aqueous phase (reverse extraction).

In the low-acid range in which hydrolysis of the trivalent species may become important, the "reverse" extraction is followed by a "direct" extraction yielding data which agree mutually.

The Pu(III) data of Fig. 1 were obtained as follows. A solution of ^{239}Pu in 16 M HNO_3 is evaporated to dryness in a small beaker by heating from above with an infra-red heat lamp. Upon disappearance of the last drop of liquid a portion of 12 M HCl is added and the evaporation repeated. Following two more evaporations with 12 M HCl the tracer is dissolved in a portion of 12 M HCl to form a plutonium feed containing principally Pu(IV). As needed, a portion of this feed is diluted with 12 M HCl and the resulting solution contacted with an equal-volume portion of 0·48 F H_2MEHP (toluene diluent). (In this system, the K for Pu(III) is approximately 0·1, that for Pu(VI) less than 0·1 and that for Pu(IV) greater than 800.) The resultant extract is scrubbed with five quadruple-volume portions of 12 M HCl to remove Pu(VI), and incidentally Pu(III). The scrubbed extract is then contacted with one or more equal-volume portions of aqueous 12 M HCl, 0·1 M in hydroquinone. This aqueous extract is contacted with a one-fourth volume portion of 0·48 F H_2MEHP to remove traces

[1] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[2] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).

of Pu(IV). The resultant tracer solution, predominately Pu(III), is diluted to the proper HCl concentration for immediate use.

The Np(VI) data of Fig. 1 were obtained as follows. A solution containing neptunium primarily in the hexavalent state is prepared by bromate oxidation in 1 M H_2SO_4. This solution is contacted with 0·48 F H_2MEHP (toluene diluent). The resultant extract is scrubbed rapidly with two equal-volume portions of 2 M HCl to remove traces of H_2SO_4 (30 sec contact times). Aliquots of the scrubbed extract are then contacted for 30 sec periods with portions of aqueous HCl of the desired concentration (reverse extraction). Following rapid removal of aliquots for analysis, each pregnant aqueous phase is mixed for 30 sec with a portion of barren 0·48 F H_2MEHP (direct extraction).

No difficulty is experienced in obtaining the Np(VI) data in the systems involving H_2SO_4, since there is no detectable formation of Np(IV).

The Np(IV) data were obtained as follows. A solution of Np primarily in the tetravalent state is prepared by making a 12 M HCl solution of the tracer 0·1 M in hydroquinone and allowing the solution to stand at room temperature for 10 min. (In such a solution Np(VI) is largely reduced to Np(IV) in less than 30 sec.) This solution is then contacted with 0·48 F H_2MEHP and the resultant extract scrubbed with barren 12 M HCl to remove traces of Np(VI). Portions of the scrubbed extract are then equilibrated against portions of aqueous HCl of the desired concentration. These reverse extraction data are confirmed by contacting the resultant pregnant aqueous phases with barren 0·48 F H_2MEHP to yield direct extraction data.

Testing of flow sheet components

In an experiment in which a synthetic feed material containing 2×10^5 counts/min of ^{237}Np (freshly separated from its daughter ^{233}Pa), 10^7 counts/min each of ^{239}Pu and ^{241}Am, and 10^6 counts/min each of ^{147}Pm, ^{155}Eu and ^{154}Eu, and ^{91}Y was processed by a single equal-volume extraction from "reducing" 6 M HCl by 0·48 F H_2MEHP (in toluene) followed by four equal-volume scrubs of the extract with aqueous 6 M HCl + 0·1 M hydroquinone, the recovered Np (yield in excess of 95 per cent) contained no detectable α-active or β-active impurity. (The extract was transferred to a fresh contactor following the second scrub.) The data indicate minimum decontamination factors of 10^5 with respect to Pu and Am and 10^4 with respect to Pm, Eu, and Y.

In a similar experiment involving ^{237}Np, ^{239}Pu and ^{233}U (single equal-volume extraction from "reducing" 12 M HCl by 0·48 F H_2MEHP followed by two equal-volume scrubs of the extract with aqueous 12 M HCl + 0·1 M hydroquinone, with change of contactor following the second scrub) minimum decontamination factors of 10^3 and 200 were shown with respect to Pu and U respectively.

Isolation of Np *from a process material*

A portion of a process material, resulting from the processing of neutron-irradiated uranium for plutonium, especially prepared for neptunium recovery was processed as follows. A 250 ml portion of this material, essentially a 0·75 M $Al(NO_3)_3$ + 1 M HNO_3 aqueous solution containing approximately 2·2 mg of ^{239}Pu and 6 mg of ^{238}U per ml and having a ratio of ^{237}Np to ^{239}Pu, by activity, of 5×10^{-5} as shown by chemical yield experiments (approximately 2·5 mg ^{237}Np in total sample), was made 0·1 M in hydroquinone and 0·1 M in KI and allowed to stand 10 min. This reduced solution was then contacted, for 3 min periods, with two 25 ml portions of 0·48 F H_2MEHP (toluene diluent).

The resultant extract (the combined solvent phases totalling approximately 50 ml) was then contacted, for 3 min periods, with six 50 ml portions of a freshly-prepared aqueous scrub 12 M in HCl and 0·1 M in hydroquinone, the extract being transferred to a fresh contactor following the second and fourth scrubs, and contacted for a 5 min period with a 50 ml portion of freshly-prepared "oxidizing" solution, 1 M in HCl and 0·2 M in $KBrO_3$, preceding the third and fifth scrubs respectively. (Without interspersion of oxidizing steps the decontamination factor with respect to uranium is limited to the range 200–700 due to the few parts per thousand of U(IV) in the U(VI).)

Samples of the extract, at each stage of the separation, were evaporated for radiometric analysis. The ^{237}Np : ^{239}Pu ratio, by activity, was determined by α-pulse analysis. The data are shown in Table 1.

RESULTS AND CONCLUSIONS

From Fig. 1 it is seen that neptunium, as Np(IV), is easily separable from U(VI), Pu(III), Am(III) and Cm(III) by use of the system 0·48 F H_2MEHP (toluene) vs.

TABLE 1.—ISOLATION OF ^{237}Np FROM A PROCESS MATERIAL

FEED: 250 ml OF AQUEOUS HNO_3 CONTAINING APPROXIMATELY 550 mg ^{239}Pu, 2·5 mg ^{237}Np AND 1500 mg ^{238}U. REDUCED FEED EXTRACTED WITH TWO 25 ml PORTIONS OF 0·48 F H_2MEHP (TOLUENE DILUENT). EXTRACT SCRUBBED WITH 6* 50 ml PORTIONS OF 12 M HCl + 0·1 M HYDROQUINONE. EXTRACT SAMPLED AFTER INITIAL EXTRACTION AND FOLLOWING SCRUBS AS $X-1$, $X-2$, ETC. YIELD OF ^{237}Np IN EXCESS OF 95 PER CENT.

Composition	Feed	Extract				
		$X-1$	$X-3$	$X-5$	$X-6$	$X-7$
total alpha (c/m)	4×10^{10}	$1{\cdot}7 \times 10^{10}$	$7{\cdot}7 \times 10^{8}$	$3{\cdot}8 \times 10^{6}$	$2{\cdot}0 \times 10^{5}$	$1{\cdot}9 \times 10^{4}$
$(^{237}Np/^{239}Pu)_{act.}$	5×10^{-5}	—	<0·01	0·7	9	>50†
$(^{237}Np/^{238}U)_{mass}$	$<2 \times 10^{-3}$	—	—	—	—	>250†

* Extract transferred to a fresh contactor following second and fourth scrubs.
† Product DF with respect to ^{239}Pu and ^{238}U, respectively: $>1 \times 10^{6}$ and $>1 \times 10^{5}$.

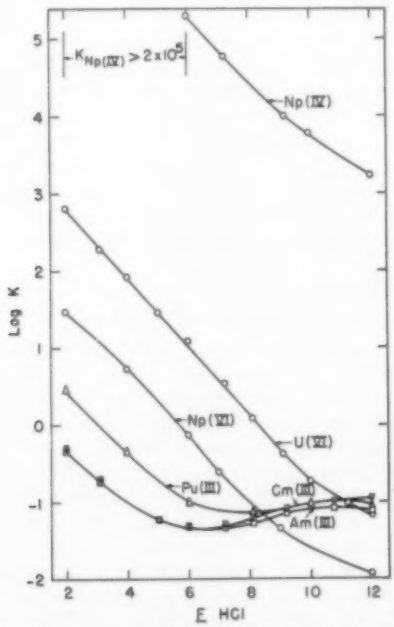

FIG. 1.—Extraction of selected actinide cations into 0·48 F H_2MEHP (toluene) as a function of HCl concentration.

12 F HCl. The K value for Np(IV) of approximately 10^3 is sufficiently large that multiple extraction, in general, should be unnecessary. The corresponding K values for U(VI), Pu(III), Am(III) and Cm(III), all approximately 10^{-1}, are sufficiently small that the removal of these elements is easily accomplished through multiple scrubbing.

It may be noted that whereas the K values for Np(IV), Np(VI) and U(VI) decrease with increasing concentration of HCl in the aqueous phase throughout the range investigated, those for Pu(III), Am(III) and Cm(III) acquire a minimum value. This minimum occurs at approximately 6–7 F HCl for the latter two elements. Consequently, the separation of Np(IV) from Am(III) and Cm(III) could be performed more effectively at 6 F HCl than at 12 F HCl. The increased effectiveness, however, is not large; and at 6 F HCl the K for U(VI) is approximately 10. Consequently, if all of the actinides of Fig. 1, but only these and no lanthanides, are present in the material from which neptunium is to be isolated, the separation is most advantageously made at 12 F HCl. If uranium is absent, then 6 F HCl is to be preferred,

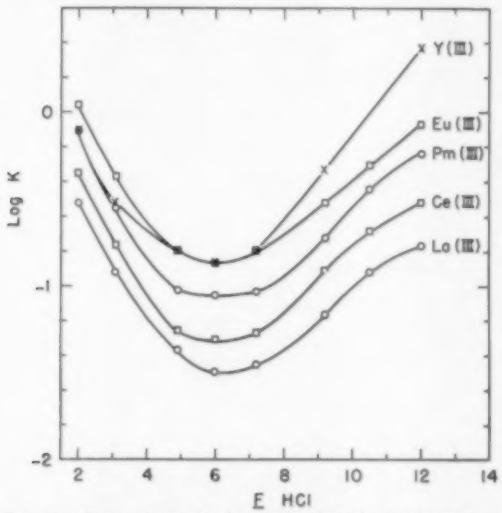

FIG. 2.—Extraction of selected lanthanide (and yttrium) cations into 0·48 F H_2MEHP (toluene) as a function of HCl concentration.

although the reduction of plutonium to Pu(III) is not achieved as readily in the 6 F HCl system as in the 12 F.

However, as seen from Fig. 2, if certain fission product lanthanides, especially Y or Eu are to be eliminated, the preferred system involves 6 F HCl. The yttrium K value of 2·4 at 12 F HCl is nearly 20 times that at 6 F HCl.

It is to be noted further, from Figs. 3 and 4, that the purification of neptunium is operationally simplified by use of a solvent more dilute than the 0·48 F H_2MEHP (toluene) solvent used in the separations described, provided that the K for neptunium remains acceptably large. The K values for all of the metallic species considered have nearly the same solvent dependency so that the pertinent β values (where β is the ratio of K_A to K_B) are nearly independent of the H_2MEHP concentration.

It is apparent that effective purification of neptunium with respect to lanthanide and actinide contaminants may be accomplished by use of systems involving the proper concentrations of H_2MEHP and HCl and the proper valence state of the contaminants. It might be assumed that efficient return of the product neptunium from the purified extract to an aqueous phase should be attained through judicious choice of these same variables.

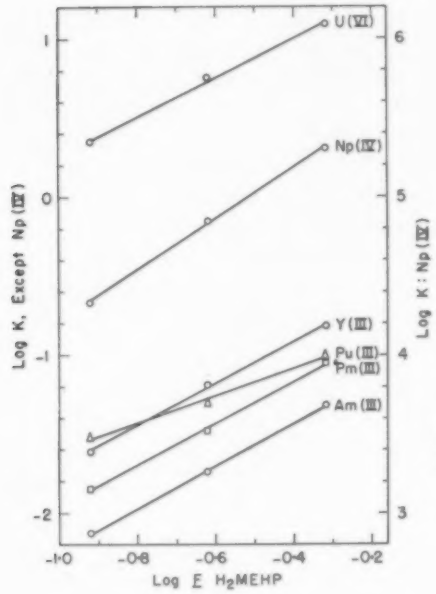

FIG. 3.—Extraction of selected actinide and lanthanide (and yttrium) cations from 6 F HCl as a function of H_2MEHP (toluene) concentration.

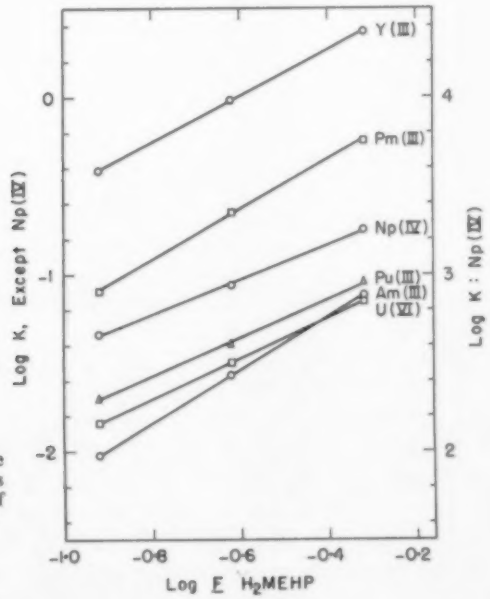

FIG. 4.—Extraction of selected actinide and lanthanide (and yttrium) cations from 12 F HCl as a function of H_2MEHP (toluene) concentration.

From Fig. 1, it is seen that Np(VI) extracts more poorly than does U(VI) in the 0·48 F H_2MEHP vs. HCl system. However, oxidation of Np(IV) to Np(VI) in a concentrated aqueous HCl solution is extremely difficult, and this difficulty is compounded by the complexing of the Np(IV) by the H_2MEHP in the organic extract. Consequently, removal of neptunium from the extract by re-extraction of Np(VI) into aqueous HCl is not promising. The data of Figs. 3 and 4 show that removal of

Np(IV) to aqueous 6 F or 12 F HCl through dilution of the extract with toluene is impractical, since the solvent dependency does not greatly exceed first power and the RK (where R is the volume ratio of extract to aqueous HCl) product therefore remains nearly constant with dilution.

Although Np(IV) may be removed from this extract quite quantitatively by contacting the extract with aqueous 2 F HF, the procedure leaves the product in a form unsuitable for use in many types of investigation. In addition, if a precipitate of neptunium fluoride forms it is likely to occlude H_2MEHP. Consequently, a means of

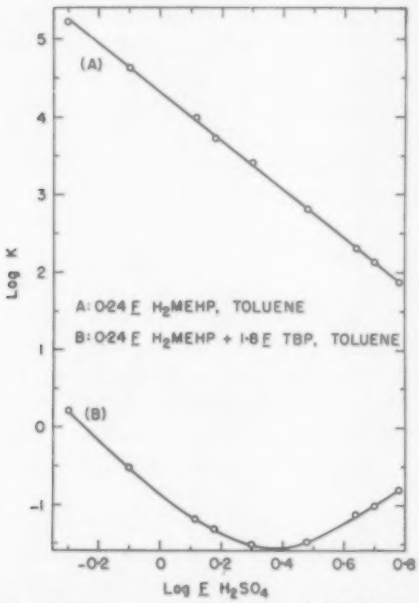

FIG. 5.—Extraction of Np(IV) into: (A) 0·24 F H_2MEHP (toluene) and (B) 0·24 F H_2MEHP + 1·8 F TBP (toluene), as a function of H_2SO_4 concentration.

de-activating the H_2MEHP was sought, so that through depressing the solvent action of H_2MEHP the K for Np(IV) might be lowered sufficiently to permit re-extraction with an aqueous mineral acid solution.

The data of Fig. 5 demonstrate the depressant action of tri-butyl phosphate, TBP, on the extractive action of H_2MEHP. In the absence of TBP, the K in the 0·24 F H_2MEHP vs. H_2SO_4 system (toluene diluent) is approximately inverse third-power dependent upon the concentration of H_2SO_4 in the aqueous phase but remains awkwardly large (approximately 75) at 6 F (12 N) H_2SO_4. By contrast, in the (0·24 F H_2MEHP + 1·8 F TBP) vs. H_2SO_4 system (toluene diluent) the K is lower by a factor approximating 10^5 throughout the 0·5–2 F H_2SO_4 range, the K reaching a minimum value of approximately 0·03 in the neighbourhood of 2 F H_2SO_4.

For removal of Np(IV), this solvent composition is approximated with sufficient accuracy by diluting the purified extract (initially 0·48 F H_2MEHP in toluene) with an equal volume of washed TBP.

In tests of the flow sheet components, separations realized are in good agreement

with calculations based on the data of Figs. 1–4. Likewise, the isolation of ^{237}Np, illustrated by the data of Table 1, has been accomplished with resultant decontamination factors (*DF*) with respect to ^{239}Pu and ^{238}U consistent with the batch tracer data.

DISCUSSION

PEPPARD *et al.*[3] have recently reported on the use of acidic esters of orthophosphoric acid as selective extractants (from dilute to moderately concentrated aqueous mineral acid) for certain tracer-level metallic cations, concluding that the dimeric $(GO)_2PO(OH)$ extractant functions in a manner analogous to that ascribed to thenoyltrifluoroacetone (HTTA), whereas it is suggested that the extraction mechanism for polymeric $(GO)PO(OH)_2$ is formally analogous to the solid resin ion exchange mechanism. Whether the extraction of metallic cations into H_2MEHP, a representative of the $(GO)PO(OH)_2$ class, from aqueous solutions 4–12 F in HCl proceeds by an "ion exchange" mechanism or by an alternative such as discrete chelation or ion pair association has not been established. However, it is of interest to note that both at 6 F HCl and 12 F HCl the apparent solvent dependency for the cations studied ranges from 1·0 power to 1·5 power, Figs. 3 and 4.

The *K* values for Np(IV), Np(VI) and U(VI) decrease with increasing HCl concentration throughout the range investigated, whereas those for the trivalent cations, with the exception of the *K* for Pu(III), decrease to a minimum value at approximately 6·5 F HCl, Figs. 1 and 2. (The minimum *K* for Pu(III) appears to occur at approximately 8 F HCl; but since all of the Pu(III) data are somewhat suspect due to the probable presence of some Pu(IV), and the difficulty of reducing Pu(IV) to Pu(III) increases with decreasing HCl concentration, the exact position of this minimum is in doubt.).

In Fig. 6, data from Figs. 1 and 2 for La(III), Am(III), Np(IV) and U(VI), considered to form in concentrated hydrochloric acid respectively, no chloride complexes, weak chloride complexes and strong chloride complexes,[4] are shown on a log–log plot. The La(III) and Np(IV) data of DIAMOND *et al.*[4] for elution peak positions in the ion exchange system, Dowex-50 sulphonic resin vs. aqueous hydrochloric acid, are included for comparison.

In the liquid–liquid extraction system, the Np(IV) and U(VI) plots may be represented as straight lines of slope approximately −7 in the 6–12 F HCl range. The La(III) and Am(III) plots are roughly parallel to each other and of negative slope in the 2–6 F HCl range. Following the minimum, at approximately 6–7 F HCl, the plots differ considerably. The La(III) plot is essentially a straight line in the 9–12 F HCl region, whereas the Am(III) plot contains a maximum in this region with the *K* at 12 F HCl being less than that at 10·5 F HCl. The curves mutually intersect at approximately 9·5 F HCl.

The ion exchange elution peak position plots for La(III) and Np(IV) bear a remarkable resemblance to the corresponding extraction plots. It should be noted that, although the La(III) and Np(IV) elution peak position plots truly intersect, whereas the corresponding extraction plots fail to do so by a large margin (the Np(IV) data being plotted on a different scale), the relative shapes of the curves are similar, and

[3] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **7**, 276 (1958).
[4] R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).

the minima in the La(III) curves occur at approximately the same concentration of hydrochloric acid.

Through reasoning analogous to that of DIAMOND *et al.*[4] a plausible explanation of the extraction data of Fig. 6 may be based on partial dehydration of the cation and on formation of chloride complexes. Assuming with DIAMOND *et al.*[4] that increasing the concentration of hydrochloric acid decreases the effective size of the cation by dehydration, a minimum such as displayed by La(III) might be expected. For a cation which is converted, to an ever increasing extent, to a non-extracting or more

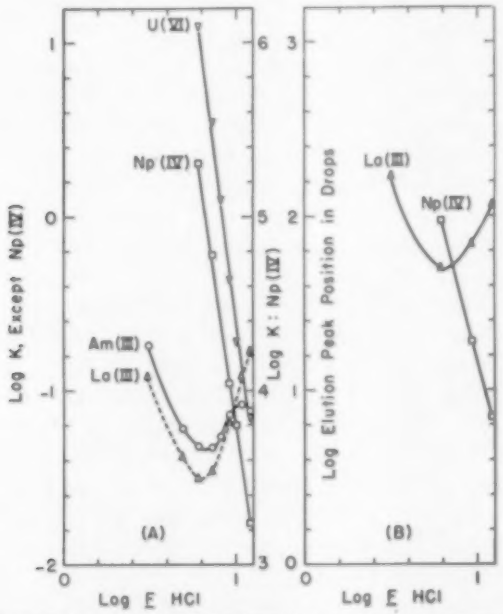

FIG. 6.—Comparative extraction behaviour, (A), and cation exchange behaviour,[4] (B), of selected cations.

poorly extracting chloride complex with increasing hydrochloric acid, a continuously decreasing K, as shown for U(VI) and Np(IV), is to be expected, although the reason for the straight line log–log plot in the high acid region is not apparent. The Am(III) plot may then be explained as due to the dehydration effect and a superimposed complexing effect in the 9–12 F HCl range.

The remaining data of Figs. 1 and 2 might be interpreted similarly, with the behaviour of Y posing a special problem. The Y curve, which is above that for Eu at 12 F HCl, converges toward the latter with decreasing concentration of HCl, crossing it in the 5–7 F HCl range and meeting the Pm curve at 2–3 F HCl. In an extension of this study, it has been noted that the curves for Ho and Er, elements 67 and 68, lie above that for Eu in the high-acid range but below in the low-acid range. (As will be reported in detail, elsewhere, the lanthanide(III) plot of log K vs. Z in the low-acid range passes through a maximum followed by a minimum, with yttrium being double-valued with respect to pseudo-Z.).

Comparison of the solvent extraction data with the ion exchange data[4] at 9 F HCl for M(III) is interesting in that the Z-effect in the one system is seen to be the

opposite of that in the other. For example, the sequence La(III), Ce(III), Eu(III) and Y(III) represents increasing tendency to be extracted by the phosphate ester but decreasing tendency to be bound by the sulfonic resin. The same effect has been noted for the Ac(III), Am(III) and Cm(III) sequence.

This reversal appears to be in accord with the observation of BREGMAN and MURATA[5] that the order of selectivity for the alkali cations, which is Li, Na, K for a sulphonic resin, is *K*, Na, Li for a phosphonic resin. BREGMAN and MURATA[5] explain this reversal on the basis of relative polarizability of ionic groups and water, as calculated by TEUNISSEN and BUNGENBERG DE JONG,[6] considering the order of polarizability to be phosphate > water > sulphate.

In an unpublished extension of this study in this laboratory, it has been found that the order of increasing extraction from a neutral aqueous chloride solution into bis (2-ethylhexyl) ortho phosphoric acid, a representative of the $(GO)_2PO(OH)$ type of solvent, is K, Na, Li while the reverse order of extraction is found for a commercially available mono (heptadecyl) sulphuric acid, a representative of the $(GO)SO_2(OH)$ type of solvent.

The high order of discrimination shown for Np(IV) with respect to U(VI), Np(VI) and various actinides (III) and lanthanides (III) led to a preliminary investigation of the behaviour of tracer-level Zr(IV), Hf(IV) and Th(IV) in H_2MEHP vs. HCl systems. In the 0·24 F H_2MEHP (toluene) vs. 12 F HCl system the *K* for each of these is in excess of 10^4, to be compared with approximately 900 for Np(IV) and 0·03 for U(VI). Consequently, the separation of Zr, Hf and Th from U(VI) is readily accomplished. Specific applications have been made in the separation of ^{234}Th from the naturally-occurring parent ^{238}U and of ^{233}U (prepared by neutron bombardment) from ^{232}Th. The dependence of *K* upon the state of oxidation of the element is demonstrated for Np in Fig. 1. The ratio of *K* values for the respective M(IV) and M(VI) states is seen to be slightly in excess of 10^5. Preliminary data indicate a ratio of at least 10^5 for the corresponding uranium *K* values.

The data of Fig. 5 also shows a ratio of approximately 10^5 for the *K* values of Np(IV) in two systems identical except for the "diluent". The diluent, TBP, interacts with the solvent, H_2MEHP, to form a composite solvent of poor extracting power for Np(IV). A similar depressant effect by TBP has been noted in the extraction of Th(IV). The nature of this TBP–H_2MEHP interaction, resulting in an anti-synergistic effect, is being investigated by infra-red techniques and others.

Through variation of the H_2MEHP concentration and HCl concentration this system should find wide application in the separation of each of the components of M(III), M(IV), and M(VI) mixtures.

Specifically with respect to isolation of neptunium, the system discussed is advantageous in that:

(1) the large *K* for Np(IV) makes multiple extraction unnecessary,
(2) the degree of discrimination in favour of Np(IV) with respect to the usual M(III) and M(VI) contaminants is high,
(3) the reduction of plutonium to Pu(III) is rapid at room temperature,
(4) the return of Np to an aqueous phase is readily accomplished, and
(5) the physical behaviour of the system is completely satisfactory.

[5] J. I. BREGMAN and Y. MURATA, *J. Amer. Chem. Soc.* **74**, 1867 (1952).
[6] P. H. TEUNISSEN and H. G. BUNGENBERG DE JONG, *Kolloid Beihefte* **48**, 80 (1938).

The mechanism of extraction of the cations by H_2MEHP and the mode of interaction between H_2MEHP and TBP resulting in a strong anti-synergistic effect pose two problems of some theoretical significance.

It should be noted that the K for any metal in a specific state of oxidation is suspect if obtained under conditions such that interference from other states of oxidation is possible. For example, the K for U(IV), determined tentatively as being in excess of 7×10^3 for a 0·48 F H_2MEHP vs. 12 F HCl system, appears to be less than 500 unless extreme care is taken to exclude U(VI). Likewise, the K for Np(IV) as reported may be too low if traces of Np(VI) or Np(III) were present. Because of the difficulty of establishing the purity, with respect to a given state of oxidation, many of the data should be considered limiting values only, since it is believed that the re-establishment of equilibrium between a set of oxidation states may be sufficiently rapid to make the technique of "scrubbing out" or "extracting" the offending species of limited value. In this connexion, the Pu(III) curve of Fig. 1 is presented only as a limiting curve, the true curve for pure Pu(III) being assumed to be below the operational curve.

It should be noted, also, that these separations are, in part, time dependent; since after several hours a very considerable fraction of the uranium is present as U(IV) in an aqueous phase initially 12 M in HCl and 0·1 M in hydroquinone.

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THE EXTRACTION OF NITRATES BY PHOSPHORYLATED REAGENTS—I

THE RELATIVE EXTRACTION RATES AND SOLVATING MECHANISMS FOR URANYL NITRATE

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Abstract—The partitioning of uranyl nitrate between a number of non-ionic phosphorylated reagents and dilute nitric acid has been measured. Experiments at varying concentrations of the extractants (S) in an inert diluent such as benzene indicate that in most cases the disolvates $UO_2(NO_3)_2\ 2S$ are formed. Non-ionic reagents containing the diphosphoryl group $\equiv P(O)—Y—(O)P\equiv$, (where Y is oxygen, methylene, or ethylene) also give disolvates when the latter are in large excess of the uranium, but when saturated with uranyl nitrate the solvates $[UO_2(NO_3)_2S]_n$, which are probably polymeric, predominate. The implications of these results are discussed. Electronegative or base weakening substituents on the phosphoryl group decrease the partition coefficient, and that obtained with triphenyl phosphate is almost six orders of magnitude lower than the partition obtained with tributyl phosphine oxide.

Preliminary experiments with di-*n*-butyl phosphoric acid, indicate that this reagent extracts uranium by a chelating mechanism accompanied by hydrogen ion liberation from solutions low in nitric acid (<3·0 M), and by a solvating mechanism similar to that with non-ionic reagents at higher aqueous acid concentrations. The structure of the uranyl dibutyl phosphate complex is discussed.

THE literature contains numerous references to non-ionic phosphorylated reagents as extractants for metallic salts,[1–4] and their application to the purification of uranium and other metals by solvent extraction has been well established. With tri-*n*-butyl phosphate (TBP) the extraction mechanism for uranyl nitrate from an aqueous into an organic phase is[1]

$$UO_2^{2+}(a) + 2NO_3^-(a) + 2TBP(o) \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP(o) \qquad (1)$$

It is also known that the extraction properties of the phosphorylated reagents are influenced by the nature of the substituents on the phosphoryl ($\equiv P{=}O$) group.[5,6] With the exception of TBP, much of the published work on the extraction properties of the other non-ionic phosphorylated reagents is limited in scope, as the practical implications in these cases were the most important issue. This report extends the available data, and the extraction behaviour of the reagents with uranyl nitrate is investigated under conditions that are thermodynamically ideal, that is by using only very dilute solutions of uranium and extractants. Investigations into the extracting properties of non-ionic diphosphoryl reagents such as pyrophosphate and diphosphonate esters are reported for the first time.

[1] R. L. MOORE, *U.S.A.E.C. Report* AECD 3196 (1951).
[2] J. C. WARF, *J. Amer. Chem. Soc.* **71**, 3257 (1949).
[3] H. A. C. MCKAY *et al.*, *J. Inorg. Nucl. Chem.* **4**, 304, 315, 321 (1957).
[4] T. V. HEALY and P. E. BROWN, AERE C/R-1970 (1956).
[5] J. KENNEDY and S. S. GRIMLEY AERE C/M-48 (1953).
[6] L. L. BURGER *J. Phys. Chem.* **62**, 590 (1958).

The extraction of hexavalent uranium by ionic dialkyl phosphoric acids from aqueous solutions of relatively low inorganic acid concentrations has been the subject of a number of reports.[7,8] As these acids are dimeric in inert diluents such as benzene,[9] and from the dependence of uranium partitions on the second power of the extractant and aqueous acid concentrations, BAES *et al.*[10] conclude that the extracting mechanism is

$$UO_2^{2+}(a) + 2(HX)_2(o) \rightleftharpoons UO_2X_2 \cdot 2HX(o) \cdot + 2H^+(a) \qquad (2)$$

The experiments reported here using di-*n*-butyl phosphoric acid (HDBP) as an extracting reagent are of a preliminary nature, but they do reveal a novel feature in that with high aqueous acid concentrations the partition isotherm is not consistent with an inverse hydrogen ion dependency. Some of the physical properties of uranyl dibutyl phosphate have been noted, and structures are postulated for this complex and the solvates formed between uranyl nitrate and the non ionic reagents.

A brief account of some of the results obtained in these investigations has already been published[11] and details of the experiments and their implications are given in this paper.

EXPERIMENTAL

Reagents

The non-ionic phosphorylated reagents used in the experiments are listed in Table 1 (see over; "Results and Discussion"). With the exception of the phenyl phosphates which were prepared at AERE the other phosphorylated reagents were obtained as commercial products from Albright and Wilson's Ltd., Birmingham, or prepared under U.K.A.E.A. contract with the same firm. These were further purified by distillation at low pressures. Precautions against explosive degradation, and polymerization during distillation, were taken with the allyl phosphate esters.[12] Distillation of the diphosphoryl derivatives resulted in appreciable pyrolysis, and in acid contaminated distillates. Analyses of the latter however revealed that they consisted of at least 99·5 per cent of the desired product. HDBP was isolated by a solvent extraction method[13] from a commercial mixture under the name "Butyl Acid Phosphate". With the exception of dibutyl hydrogenphosphonate, which is rapidly hydrolysed by alkali, stock solutions of the non-acidic reagents in benzene were washed with sodium carbonate (0·25 M), and water to remove traces of acid pyrolytic products. Suitable aliquots of these solutions were then diluted with benzene to the concentrations used in the equilibrium experiments. Uranyl dibutyl phosphate $UO_2[(BuO)_2PO_2]_2$ was prepared as previously described.[8] Uranyl dibutyl phosphinate $UO_2[Bu_2PO_2]_2$ was prepared by the addition of an aqueous solution of dibutyl phosphinic acid ($Bu_2P(O)OH$; 5 per cent W/V), which had been neutralized to pH 6·0 with ammonium hydroxide, to an aqueous solution of uranyl nitrate (0·05 M). The light yellow precipitate of the phosphinate was repeatedly washed with warm water and vacuum dried at room temperature over phosphorus pentoxide. (Found for uranyl dibutyl phosphinate U, 38·0, P, 9·91; $C_{16}H_{36}O_6P_2U$ requires U, 38·1, P, 9·93 per cent.) Exposure of the phosphate and phosphinate preparations to light results in photochemical decomposition and in the production of a greenish tinge characteristic of U(IV) and, a rancid odour due probably to butyric acid. On account of this the solids were stored in stoppered bottles in the dark. Even then the odour of butyric acid was detectable after a few weeks.

Measurements

Standard benzene solutions of the extractants (25 ml; $<0{\cdot}19$ M) were equilibrated in a thermostat ($22° \pm 1°C$) with nitric acid (0·5 M), and then with an equal volume of uranyl nitrate solution

[7] D. C. STEWART and F. E. HICKS, UCRL-861 (1950).
[8] C. A. BLAKE *et al.*, *U.S.A.E.C. Report* ORNL-1903 (1955); ORNL-2172 (1956).
[9] D. F. HILL and F. J. LEITZ, HW-19155 (1950).
[10] C. F. BAES, JR., R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).
[11] J. KENNEDY, *Chem. & Ind.* 950, (1958).
[12] ANON., *Chem. Engng. News* **34**, 52 (1950).
[13] J. KENNEDY and S. S. GRIMLEY, AERE CE/R-968 (1953).

($8{\cdot}4 \times 10^{-4}$ M) in nitric acid (0·5 M). The nitric acid was used to maintain a constant ionic strength in the aqueous phase and to prevent hydrolysis of the uranyl ion. Equilibrium was attained in less than 10 min. though shaking was usually continued for 20 min. The uranium in the aqueous phase was then estimated colorimetrically or by fluorimetry and that in the organic phase in a similar manner after extraction into an aqueous solution of sodium carbonate. Partition coefficients (D_u) are defined as the equilibrium uranium concentration in the organic phase divided by that in the aqueous phase. Benzene solutions of the extractants (0·19 M) were saturated with uranyl nitrate by shaking with excess solid hexahydrate.

Partition data for HDBP in benzene were obtained by equilibrating benzene solutions of the latter (20 ml; 0·14 M) with solutions of uranyl nitrate (50 ml; 0·018 M) in nitric acid at varying concentrations (0–10 M).

The viscosities of uranyl dibutyl phosphate solutions in benzene were measured using standard procedures. As noted elsewhere[10] with solutions of uranyl di-(2-ethylhexyl) phosphate in *n*-hexane, the viscosities of these benzene solutions, decrease on standing.

RESULTS AND DISCUSSIONS

The partition coefficients (D_u) obtained for 0·19 M solutions of the non-acidic reagents in benzene are listed in order of decreasing magnitude in Table 1.

It was found in separate experiments that D_u values were independent of variations in the initial aqueous phase uranium concentration between $4{\cdot}2 \times 10^{-4}$ M and $1{\cdot}68 \times 10^{-3}$ M, with TBP, dibutyl butylphosphonate, and dibutyl hydrogen-phosphonate when these were 0·19 and 0·0475 M in benzene. This indicates that both phases are ideal with respect to uranium, and that this assumption is probably valid also for the other systems listed. As is evident, the relative order of extraction of uranium by the tributyl substituted monophosphoryl derivatives is phosphine oxide > phosphinate > phosphonate > phosphate. A similar order has been published by BURGER[6] but the progressive reduction in D_u is not so pronounced as that reported here. This difference can be attributed to greater deviations from ideality in the systems previously investigated,[6] as a result of using higher concentrations of uranium and extracting reagents.

Values of D_u with tri-*iso*-butyl phosphate are the same as those with TBP, while those obtained with tri-*sec*-butyl phosphate are slightly higher. The value of D_u decreases as the butyl groups in TBP are replaced by the unsaturated allyl groups, and a still more pronounced reduction is observed with phenyl groups as substituents. The lowest partition in the series ($D_u = 6{\cdot}7 \times 10^{-4}$) is obtained with triphenyl phosphate, and contrasts strongly with that obtained with tributyl phosphine oxide ($D_u = 3{\cdot}8 \times 10^{2}$). With the exception of dibutyl hydrogen-phosphonate $(BuO)_2P(O)H$, D_u with monophosphoryl derivatives decreases as the electronegativity of the substituents on the phosphoryl group increases.

The observed partition order $(BuO)_3P(O) > (BuO)_2P(O)H$ might appear anomalous, as the reverse would be expected from the relative electronegativities oxygen > hydrogen. It is however consistent with the basicity order phosphoric acid, $(HO)_3P(O)$; $pK_a^1 = 2{\cdot}1$, > phosphorus acid $(HO)_2P(O)H$; $pK_a^1 = 1{\cdot}2$. The relative reduction in the basicity of the latter, (and in its esters as is evident from partition data), can be attributed to an incremental nuclear charge on the phosphorus due to penetration of its electronic shell by the proton of the hydrogen, which in turn results in greater restraint on the donor electrons of the ligand.[14]

[14] W. A. WATERS, *Physical Aspects of Organic Chemistry* p. 252. Routledge and Kegan Paul, London (1953).

The low D_u values obtained with the phenyl phosphate, and the pyrophosphate, prevented their accurate determination at reagent concentrations lower than 0·19 M in benzene. With all the other mono- and di-phosphoryl reagents in Table 1, D_u is

TABLE 1.—COLUMN 2—PARTITION COEFFICIENTS (D_u) FOR URANYL NITRATE BETWEEN NON-IONIC PHOSPHORYLATED EXTRACTANTS IN BENZENE (0·19 M) AND AQUEOUS NITRIC ACID (0·5 M). COLUMN 3—MOLE RATIO OF PHOSPHORYLATED EXTRACTANT TO URANIUM (S : U) IN BENZENE SOLUTIONS OF THE EXTRACTANTS (0·19 M) WHICH ARE SATURATED IN URANYL NITRATE

Reagent and chemical formula	D_u	S : U
Tributyl phosphine oxide $Bu_3P(O)$	380	2 : 1
Butyl dibutyl-phosphinate $(BuO)Bu_2P(O)$	120	2 : 1
Dibutyl butyl-phosphonate $(BuO)_2$ Bu P(O)	10·0	2 : 1
Tetrabutyl ethylene-diphosphonate $(BuO)_2$ $P(O)(CH_2)_2(O)P(OBu)_2$	5·7	1 : 1
Tetrabutyl methylene-diphosphonate $(BuO)_2P(O)CH_2{\cdot}(O)P(OBu)_2$	1·0	1 : 1
Tri-*sec*-butyl phosphate $(sec\text{-}BuO)_3P(O)$	0·54	2 : 1
Tributyl phosphate (TBP) $(BuO)_3P(O)$	0·25	2 : 1
Tri-*iso*-butyl phosphate $(iso\text{-}BuO)_3P(O)$	0·25	2 : 1
Dibutyl allyl phosphate $(BuO)_2AOP(O)$	0·14	2 : 1
Dibutyl hydrogen-phosphonate $(BuO)_2$ HP(O)	0·12	2 : 1
Diallyl butyl phosphate $(AO)_2(BuO)P(O)$	0·032	2 : 1
Triallyl phosphate $(AO)_3P(O)$	0·018	2 : 1
Dibutyl phenyl phosphate $(BuO)_2(PhO)$ P(O)	0·0035	2 : 1
Tetrabutyl pyrophosphate $(BuO_2P(O)$ $O(O)(OBu)_2$	0·001	1 : 1
Triphenyl phosphate $(PhO)_3$ P(O)	0·00067	~22 : 1

proportional to the square of the reagent concentration [*S*], in the region 0·0475 M–0·19 M. This indicates that the extraction mechanism is

$$UO_2^{2+}(a) + 2NO_3^-(a) + 2S(o) \rightleftharpoons UO_2(NO_3)_2\,2S(o) \qquad (3)$$

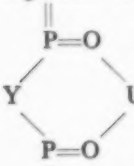
With the exception of triphenyl phosphate (extractant to uranium $\simeq$22 : 1) the 2 : 1 extractant to uranium ratio obtained with solutions of the mono-phosphorylated reagents which have been saturated in uranyl nitrate (Table 1) is also strong supporting evidence for this mechanism. This method of deducing the extraction mechanism from the solubility of uranyl nitrate in solutions of reagents is not always reliable.

As will be shown, from partition data in Part II of this series,[15] the solvated species in triphenyl phosphate systems is $UO_2(NO_3)_2 \cdot 3S$. The 22 : 1 ratio obtained with triphenyl phosphate (Table 1) does not therefore imply the formation of the solvate $UO_2(NO_3)_2 \cdot 22S$ which is anyway most unlikely, but is probably the result of the very weak co-ordinating properties of the extractant compared to water, which it cannot displace from the co-ordination sphere of the uranium as effectively as the other reagents.

The solvates with dibutyl hydrogen phosphonate and those preceding it in Table 1 are anhydrous, as is shown by Karl Fischer titrations of benzene solutions of these extractants which were saturated in uranyl nitrate. In these instances the decrease in D_u as the electronegativity of the phosphoryl group substituents is increased is probably, in the main, the result of a consequent (and expected) reduction in the stability of the solvated complexes. This indicates that phosphoryl oxygens are the only electron donors in the extractants. That alkoxy oxygens are included in the co-ordination sphere of the uranium is unlikely in view of the continuously increasing stability of the solvate when these oxygens are removed as is evident from the extraction sequence phosphine oxide > phosphinate > phosphonate > phosphate obtained with the monophosphoryl reagents. This implies that the latter behave as monodentate ligands in the solvation of uranyl nitrate.

There is considerable evidence for attributing octa-co-ordination to hexavalent uranium.[16] In crystalline rubidium uranyl trinitrate, $Rb^+[UO_2(NO_3)_3]^-$, two of the oxygens in each nitrate are assumed to partake in co-ordination with the uranium.[17] Octa-co-ordination of uranium can also be achieved in the neutral complex $UO_2(NO_3)_2\,2S$, if S is monodentate and the nitrate ligands are bidentate, as in the anionic trinitrato complex.

In the absence of steric hindrance, a ring or chelate complex as is formed between a metal and a bidentate ligand is more stable than the complex with a mono-dentate analogue, of similar basicity.[18] Diphosphoryl reagents containing the group $=P(O)Y(O)P=$ (where Y is oxygen, methylene or ethylene) might therefore be regarded as potential bidentate ligands which could give the chelate complex



$UO_2(NO_3)_2$ with uranyl nitrate. Analogous structures have been postulated for the pyrophosphate complexes of uranyl and other cations.[19,20] However, in Table 1, the relative partition sequence that is observed with diphosphoryl extractants, and some typical monophosphoryl analogues, is dibutyl butylphosphonate > tetrabutyl ethylenediphosphonate > tetrabutyl methylenediphosphonate > TBP ≫

[15] T. V. HEALY, J. KENNEDY and G. M. WAIND, *J. Inorg. Nucl. Chem.* **10**. 137 (1959).
[16] L. SACCONI and G. GIANNONI, *J. Chem. Soc.* 2368 (1954).
[17] G. H. DIEKE and A. B. F. DUNCAN, *Spectroscopic Properties of Uranium Compounds*. McGraw Hill, New York (1949).
[18] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds*. Prentice-Hall, New York (1952).
[19] C. VOEGTLIN and H. C. HODGE, *Pharmacology and Toxicology of Uranium Compounds* Pt III. McGraw-Hill, New York (1953).
[20] J. R. VAN WAZER and D. A. CAMPANELLA, *J. Amer. Chem. Soc.* **72**, 655 (1950).

tetrabutyl pyrophosphate. The decreased stability of the pyrophosphate solvate compared to that with TBP is not by itself sufficient evidence against a chelate structure for the former, as the reduction in stability which would probably be incurred by the electronegative bridging oxygen in the pyrophosphate ester may numerically exceed the increment in stability from chelate formation in its complexes. On the other hand, the bridging carbon atoms in the methylene- or ethylenediphosphonate should not adversely affect the basicity of the ligand. The observed order phosphonate > diphosphonate does therefore suggest that, if chelates are formed, they are not as stable as was anticipated. The relationship $D_u \alpha [S]^2$ is valid for the diphosphonates when these are in considerable excess of the uranium, and implies disolvate formation, whereas if chelation did occur monosolvates and the relationship $D_u \alpha [S]$ would be expected. Also, scale models of the pyrophosphates and the diphosphonates indicate that the phosphoryl groups converge and their oxygens slightly overlap. This indicates that a ring structure involving both the phosphoryl oxygens in the uranium co-ordination sphere would be strained. The evidence therefore suggests that only one of these oxygens partakes in co-ordination when the solvating reagent is in considerable excess of the metal and the section of the ligand containing the other phosphoryl oxygen, that is $—Y(O)\cdot P(OBu)_2$, functions only as an electronegative substituent, and thereby reduces the stability of the solvates compared to those formed with dibutyl butylphosphonate. As would be expected in such a structure, the negative inductive effect of this substitution is greatest with the pyrophosphate which contains a bridging oxygen as well as the alkoxy and phosphoryl oxygens in the substituents. It is less in the methylenediphosphonate where the bridging oxygen is replaced by a less electronegative carbon, and least in the ethylenediphosphonate where the distance between the phosphoryl groups is greatest.

The 1 : 1 solvent to uranium ratio obtained with diphosphoryl systems which have been saturated with uranyl nitrate (Table 1) may indicate chelate formation under these conditions. Preliminary viscosity measurements on these systems[21] do however lend support to the alternative polymeric structure

$$[UO_2(NO_3)_2(O)PYP(O)]_n.$$

The uranyl dibutyl phosphate complex $UO_2(DBP)_2$, is only slightly soluble in water (2×10^{-4} M), in anhydrous ether (1×10^{-5} M), and in odourless kerosene and *n*-hexane ($<10^{-5}$ M). It is soluble in pyridine, in HDBP and in solutions of these reagents in kerosene or *n*-hexane. In contrast with HDBP it is only slightly soluble in TBP. Its solubility in HDBP–kerosene varies linearly with the HDBP content of the kerosene and the HDBP : $UO_2(DBP)_2$ ratio in these solutions is 10 : 1. This relationship is valid for concentrations ranging from $9{\cdot}5 \times 10^{-4}$ M to 2·4 M in HDBP. The complex dissolves on heating in *cyclo*hexane and gives a viscous solution from which it separates again on standing at room temperature. The clear supernatant contains very little uranium (ca. 10^{-4} M). The complex is soluble in all proportions in benzene, and the initial stages of solution are characterized by a considerable absorption of benzene by the solid phase. These solutions are highly viscous, and a marked reduction in their viscosity is caused by the addition of HDBP, pyridine or butyric acid. The viscosity of the solutions also decreases on standing, and more rapidly in the light than in the dark. This decrease is accompanied by the production of a rancid

[21] J. KENNEDY. Unpublished work.

odour characteristic of butyric acid, and the latter is probably the main reason for the viscosity reduction. The viscosities of solutions of the complex in benzene containing varying concentrations of HDBP are given in Table 2. These solutions had been standing for 4 hr and the viscosities quoted are lower than would have been obtained with freshly prepared solutions. A parallel behaviour is observed for solutions of uranyl di-(2-ethyhexyl) phosphate in *n*-hexane,[10] though uranyl dibutyl phosphate is almost insoluble in this solvent.

TABLE 2.—VISCOSITIES OF A BENZENE SOLUTION OF URANYL DIBUTYL PHOSPHATE (0·087 M) IN THE PRESENCE OF FREE DIBUTYL PHOSPHORIC ACID

Molar concentration of HDBP	Viscosity (centipoises)
0	30·3
$4{\cdot}4 \times 10^{-4}$	8·4
$8{\cdot}8 \times 10^{-4}$	5·22
$1{\cdot}76 \times 10^{-3}$	2·64
$8{\cdot}8 \times 10^{-3}$	1·136
$4{\cdot}36 \times 10^{-2}$	0·806
$2{\cdot}62 \times 10^{-1}$	0·79

The high viscosity of these solutions indicates that the complex is a polymer. A monomeric chelate structure, such as that depicted in Fig. 1(a), would imply hexa-co-ordination for the central uranium atom, and the polymer formation is therefore probably due to octa-co-ordination of the uranium being achieved as a result of additional uranium to oxygen linkages as in Fig. 1(b). Here one oxygen in each ligand partakes in the co-ordination sphere of two uranium atoms. Alternative polymeric structures involving the butoxy oxygens are unlikely, as separate experiments have shown that benzene solutions of uranyl dibutyl phosphinate $UO_2[Bu_2PO_2]_2$ (which does not contain butoxy oxygens) are also viscous.

The reduction in viscosity of solutions of the complex on the addition of HDBP, pyridine or butyric acid, could result through the polymer chain being broken due to the co-ordination requirements of some or all of the uranium atoms being supplied by donor atoms (oxygen or nitrogen) in the added reagents. In their presence the solvated species is probably that depicted in Fig. 1(c) where L represents a molecule of the added reagent and $x \leqslant n$ in Fig. 1(b). In the limit when the reagents are in excess, the monomeric species Fig. 1(d) predominates. BAES *et al.*,[10] who were dealing with solutions of uranyl di-(2-ethylhexyl) phosphate in the presence of di-(2-ethylhexyl) phosphoric acid, have suggested polymeric structures in which the uranium is hexa-co-ordinated. In order to give uranium a co-ordination number of eight, structures analogous to those in Fig. 1 (c and d) were postulated by the referee to their paper, for the solvated species in the presence of the free acid.

The extraction of hexavalent uranium by HDBP from an aqueous solution of uranyl nitrate into a benzene phase is accompanied by the liberation of one mole of nitric acid per equivalent extracted. This indicates that the extraction mechanism under conditions of low aqueous phase acidity is probably in accordance with reaction

(2), as postulated by BAES *et al.*[10] The distribution coefficient for uranium between HDBP in benzene for different concentrations of nitric acid is given in Fig. 2.

The initial decrease in D_u for the HDBP system from 125 at 0·1 M HNO_3 to 4 at 3 M HNO_3 is qualitatively consistent with the expected inverse relationship to the aqueous phase acidity. However, for D_u values greater than 10, insufficient HDBP is present in the organic phase to give the monomeric solvated complex $UO_2(DBP)_2 \cdot 2HDBP$ as demanded by equation (2), and accordingly the extraction mechanism

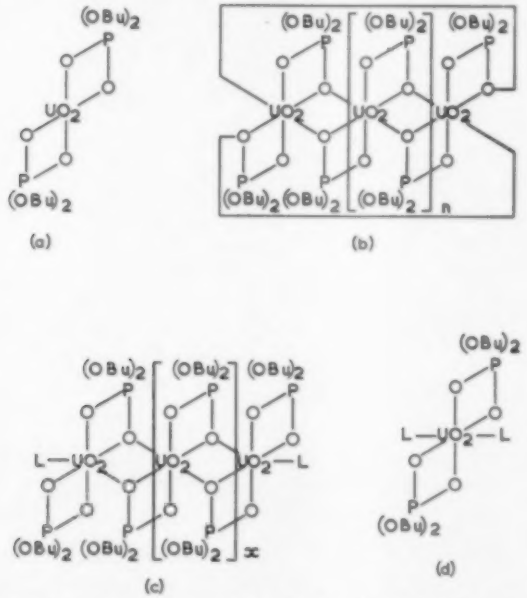


FIG. 1.—Postulated structures for uranyl dibutyl phosphate. (a) This is unlikely (see text), (b) polymeric structure in the absence of free complexing agent, (c) polymeric structure in the presence of free complexing reagent (L), ($x < n$), (d) monomeric structure in the presence of excess of complexing reagent In these structures the uranyl ion is linear and the uranyl oxygens above and below the plane of the paper.

under these conditions is likely to be governed by the formation of polyuranyl species, (Fig. 1(c), $x > 1$).

$$xUO_2^{2+}(a) + (x+1)\,(HDBP)_2(o) \rightleftharpoons [UO_2(DBP)_2]_x\,2HDBP(o) + 2xH^+(a) \quad (4)$$

The subsequent increase in D_u as the acid concentration is increased from 3 M to 7 M is not consistent with equations (2) or (4). It does however indicate a change in the extraction mechanism from a hydrogen ion to a nitrate ion dependency.

As the shape of the extraction isotherm from 3 M to 10 M HNO_3 is similar to that obtained with TBP[22] a probable extraction mechanism is

$$UO_2^{2+}(a) + 2NO_3^-(a) + (HDBP)_2(o) \rightleftharpoons UO_2(NO_3)_2 2HDBP(o) \quad (5)$$

It has also been shown,[23] that HDBP like TBP[24] extracts nitric acid, and the

[22] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).
[23] P. G. M. BROWN *et al.*, *Second International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1958, 15/P/31.
[24] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).

reduction in D_u at acid concentrations above 7 M is evidently due to a competing hydrogen bonding reaction such as

$$(HDBP)_2(o) + 2HNO_3(a) \rightleftharpoons 2HDBP \cdots HNO_3(o) \qquad (6)$$

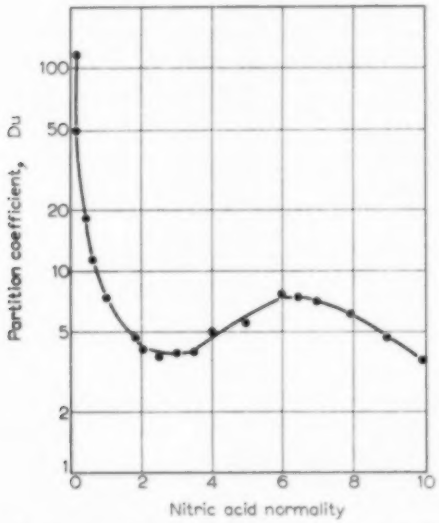


FIG. 2.—Variation of D_u with nitric acid concentrations for 0·14 M HDBP in benzene, using 20 ml organic phase, and 50 ml aqueous phase, and an initial uranium concentration of 0·018 M.

It is, however, likely that mechanisms (3) and/or (4) also occur to some extent at high acid concentrations, and the D_u values obtained are probably higher than if the extraction mechanism was confined to that of nitrate ion dependency.

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THE EXTRACTION OF NITRATES BY PHOSPHORYLATED REAGENTS—II

THE RELATIVE EXTRACTION RATES OF URANYL, COBALTOUS, AND SODIUM NITRATES WITH PHOSPHATE ESTERS

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Abstract—The partition of uranyl, cobaltous, and sodium nitrate between non-ionic phosphate esters and water has been measured, and the deviations from ideality which occur at high nitrate concentrations in the organic phase have been used to obtain solvation numbers for the extracted salts. With tri-*n*-butyl phosphate (TBP), the extracted species are the di-solvates, $UO_2(NO_3)_2 \cdot 2TBP$, and the tri-solvates $Co(NO_3)_2 \cdot 3TBP$ and $NaNO_3 \cdot 3TBP$. Tri-solvates are also formed between uranyl nitrate and weak phosphate ester extractants such as diphenyl butyl and triphenyl phosphates.

IN Part I of this series[1] it was shown that a large number of non-ionic reagents containing the phosphoryl group ($\equiv P = O$) extract uranyl nitrate as the di-solvate $UO_2(NO_3)_2 \cdot 2S$ where S is a mole of extractant. This was established from partition data for systems in which the extractant was diluted with benzene, the partition coefficients being proportional to the square of the extractant activities. The use of very dilute solutions of uranyl nitrate (initial aqueous concentration $8{\cdot}4 \times 10^{-4}$ M) and extractants ($\lesssim 0{\cdot}19$ M) also permitted the simplifying assumption that their activities in both phases were equal to their concentrations. In a number of cases, however, partition coefficients measured under these conditions were too low to permit an accurate estimate of their variation with the extractant concentration.

As shown elsewhere by GLUECKAUF *et al.*[2] solvation numbers for uranyl nitrate can be deduced from partition data obtained with undiluted extractants such as ethers, ketones, and esters of carboxylic acids. This method has been applied here to obtain solvation numbers for inorganic nitrates in undiluted phosphate ester extractants. In addition, modifications of the method were used to obtain solvation numbers when the extractants were diluted with an inert diluent such as benzene or carbon tetrachloride; this was necessary in the case of extractants such as triphenyl phosphate which are solids at room temperature.

EXPERIMENTAL

Materials

The phosphate extractants used, viz. tri-*n*-butyl phosphate (TBP), dibutyl phenyl phosphate (DBPP), diphenyl butyl phosphate (DPBP) and triphenyl phosphate (TPP), were obtained commercially or prepared at A.E.R.E. TBP was purified as described elsewhere.[3] DBPP and DPBP were redistilled (b.p. 184°/15 mm and 180°/5 mm respectively). Solid TPP was dissolved in carbon

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[1] T. V. HEALY and J. KENNEDY, *J. Inorg. Nucl. Chem.* **10**, 128 (1959).
[2] E. GLUECKAUF, H. A. C. MCKAY and A. R. MATHIESON, *Trans. Faraday Soc.* **47**, 437 (1951).
[3] J. KENNEDY and S. S. GRIMLEY, AERE/C/R-968 (1952).

tetrachloride, washed with dilute alkali and then with water, and after removal of the carbon tetrachloride at low pressures the TPP residue was distilled (b.p. 245°/11 mm). The dibutyl ether of diethylene glycol (dibutyl carbitol—DBC) was purified by a method outlined by MCKAY and MATHIESON.[4] Aqueous solutions of uranyl, cobaltous, and sodium nitrate were prepared from salts which had been repeatedly recrystallized from water; solutions of cobalt and sodium nitrate were labelled with their β-active isotopes (^{60}Co and ^{24}Na). Water contents of organic systems were obtained by Karl Fischer titration.

Partition measurements

Equilibrations were carried out in a thermostat, using pure extractants, or the latter diluted to various mole fractions in benzene or carbon tetrachloride. The salt contents of the phases were assayed radiometrically in the case of cobaltous and sodium nitrate. The uranyl nitrate was assayed colorimetrically as previously described.[1,5]

Vapour-pressure measurements

The extractant was introduced through a side-arm into a sample tube fitted with a breaker seal. After weighing the extractant, the diluent was introduced, the side-arm sealed, and the tube reweighed. It was then sealed on to a manometer attached to a vacuum line, with a mercury cut-off. After freezing the solution the apparatus was evacuated, and the tube immersed in a water bath at 25 ± 0·01°C. This procedure was repeated until a constant pressure reading was obtained. A correction for the diluent vapour in the apparatus was applied to the mole fraction of the extractant as calculated from the weights of extractant and diluent taken.

RESULTS AND DISCUSSION

Partition with pure extractants

The results at 25°C for the extraction from water of uranyl, cobalt, and sodium nitrates by the phosphate esters are given in Table 1; m_{aq} and m_{org} are the aqueous

TABLE 1.—PARTITION DATA FOR NITRATES BETWEEN UNDILUTED EXTRACTANTS AND WATER

Uranyl nitrate

TBP			DBPP		DPBP	
m_{aq}	m_{org}	Density of organic phase	m_{aq}	m_{org}	m_{aq}	m_{org}
0·0293	0·0155	0·984	0·033	0·00275	0·155	0·00710
0·0400	0·0399	—	0·0579	0·0113	0·204	0·0178
—	0·0610	—	0·101	0·0361	0·303	0·0374
0·0604	0·103	—	0·187	0·127	0·390	0·0760
—	0·165	1·027	0·290	0·276	0·561	0·209
0·0847	0·266	—	0·490	0·610	0·852	0·410
—	0·347	1·063	0·614	0·761	0·875	0·434
0·149	0·578	—	(satd.)	1·91	1·17	0·698
—	0·830	1·192			1·79	1·10
0·250	0·987	—			(satd.)	1·24
0·380	1·31	1·320				
0·782	1·63	1·400				
1·00	1·71	1·421				
(satd.)	1·89	1·476				

[4] H. A. C. MCKAY and A. R. MATHIESON, *Trans. Faraday Soc.* **47**, 428 (1951).
[5] A. A. SMALES and E. FURBY, AERE C/R-344 (1950).

TABLE 1 (*contd.*)

Cobalt nitrate

TBP			DBPP		DPBP	
m_{aq}	m_{org}	Density of organic phase	m_{aq}	m_{org}	m_{aq}	m_{org}
0·264	0·000380	—	2·62	0·0054	3·36	0·0046
0·360	0·00101	—	2·91	0·0138	3·45	0·0055
0·775	0·00650	0·9773	3·17	0·0180	4·06	0·0180
0·990	0·0144	—	3·50	0·0324		
1·04	0·0170	—	4·06	0·0610		
1·15	0·0282	0·9798				
1·27	0·0450	—				
1·43	0·0681	—				
1·79	0·116	0·9914				
2·63	0·321	—				
2·78	0·362	1·0205				

Sodium nitrate

TBP	
m_{aq}	m_{org}
0·100	0·00011
0·252	0·00042
0·513	0·00156
1·035	0·00430
2·15	0·0101
6·06	0·0262
(satd.)	0·0480

and organic salt molalities respectively. Where solutions were measured by volume, the densities of the organic phases are included. Partition data for sodium nitrate are confined to the TBP system. The greater extracting powers of the phosphate esters are compared in Fig. 1 with those of a few of the better non-phosphorylated organic extractants, viz. DBC, methyl *iso*butyl ketone (MIK), and *i*-amylacetate.[2] Viscosity and conductivity measurements of solutions of the nitrates in the phosphate extractants show that in all cases the salts were less than one per cent ionized in the organic phase.[6] This should make the extraction data for these reagents amenable to the treatment previously applied to that of uranyl nitrate in ethers, esters of carboxylic acids, and ketones.[2] The partition equilibrium coefficient $(\text{nitrate})_{org}/(\text{nitrate})_{aq}$ = constant (K), has been rewritten $Km^x\gamma^x = m_{org}\gamma_{org}$. For dilute solutions of salts in the organic phase γ_{org} is unity and

$$x \log m\gamma + \log K = \log m_{org} \qquad (1)$$

[6] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).

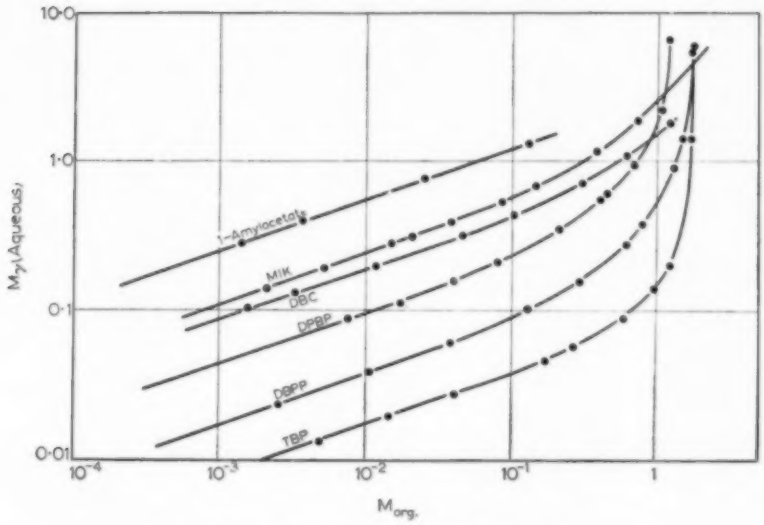

FIG. 1.—Uranyl nitrate partition with undiluted extractants.

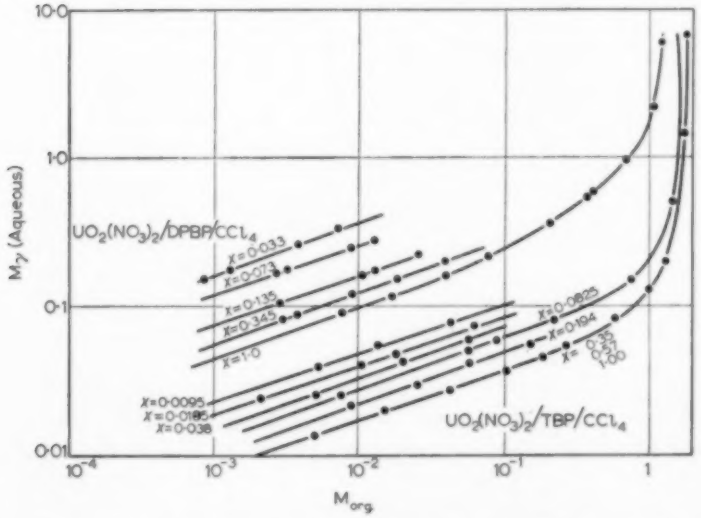

FIG. 2.—Metal nitrate partition with extractants at different mole fractions (X) in organic diluents.
(1) $UO_2(NO_3)_2$/DPBP/CCl_4
(2) $UO_2(NO_3)_2$/TBP/CCl_4

Logarithmic plots of $m\gamma$ vs. m_{org} for uranyl and cobaltous nitrates ($x = 3$) using undiluted extractants are given in Figs. 1–6 along with those obtained with diluted extractants (see below) and similar plots for sodium nitrate ($x = 2$) are given in Fig. 5. The expected slopes of a third and half are obtained up to $m_{org} \simeq 0{\cdot}1$. For all the systems, the deviations from linearity at $m_{org} > 0{\cdot}1$ in plots of $m\gamma$ vs. m_{org}

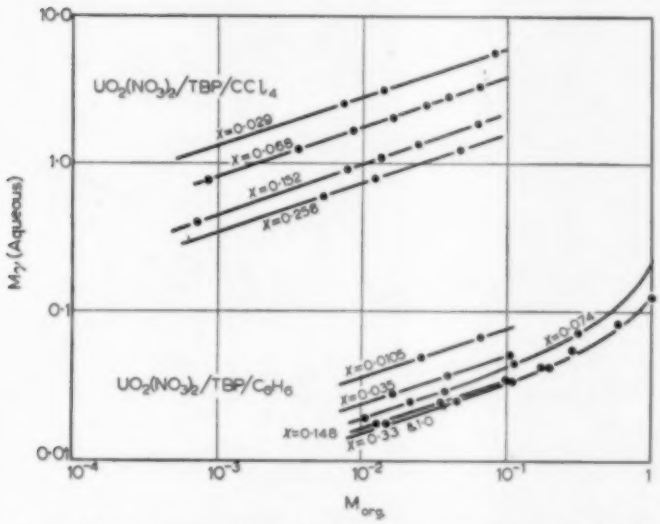

FIG. 3.—Metal nitrate partition with extractants at different mole fractions (X) in organic diluents.
(1) $UO_2(NO_3)_2$/TPP/CCl_4
(2) $UO_2(NO_3)_2$/TBP/C_6H_6

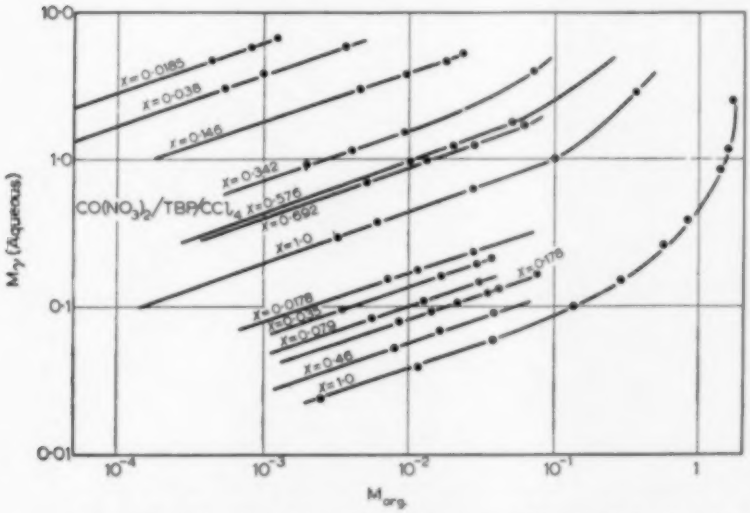

FIG. 4.—Metal nitrate partition with extractants at different mole fractions (X) in organic diluents.
(1) $Co(NO_3)_2$/TBP/CCl_4
(2) $UO_2(NO_3)_2$/DBPP/CCl_4

(Figs. 1–6), have been used to calculate solvation numbers n' as described by GLUECKAUF *et al.*[2] using the equation

$$m^3\gamma^3(S)^{n'} = K'(m_{org}) \tag{2}$$

assuming that the organic phase behaves ideally. The results obtained from this

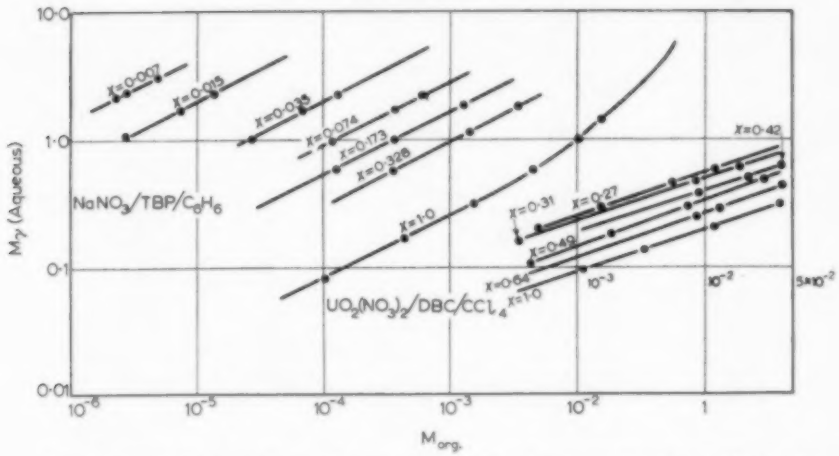

FIG. 5.—Metal nitrate partition with extractants at different concentrations in organic diluents.
(1) $NaNO_3/TBP/C_6H_6$ (TBP conc. in % V/V)
(2) $UO_2(NO_3)_2/DBC/CCl_4$ (DBC conc. in mole fraction (X))

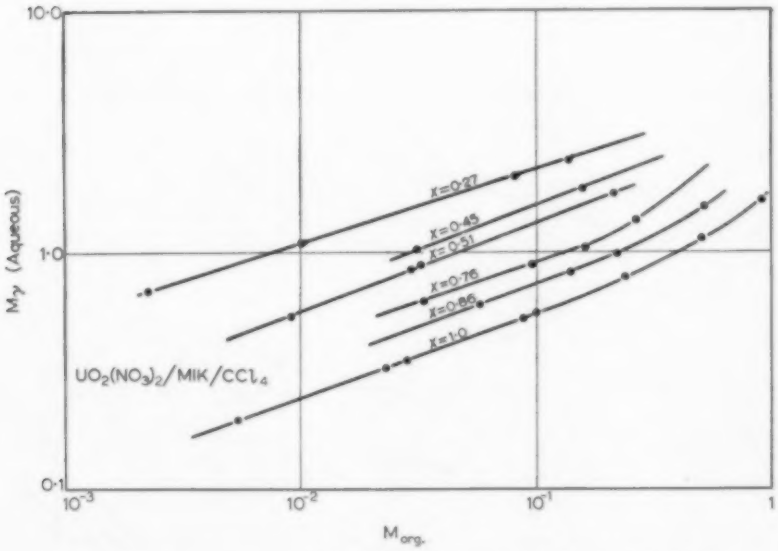

FIG. 6.—Metal nitrate partition with MIK at different mole fractions (X) in CCl_4.

treatment are given in Table 2 together with those for the dilute solutions of extractant in diluent.

The thermodynamic partition coefficients $\left(K = \frac{m_{org}}{(m\gamma)^x}\right)$, and the heat content and entropy changes (ΔH and ΔS) in transferring uranyl and cobaltous nitrates from water to pure TBP and DBPP (calculated from partition data obtained at 0°C and 50°C) are given in Table 3. The sequence of partition coefficients (K) for the three nitrates is $UO_2(NO_3)_2 \gg Co(NO_3)_2 > NaNO_3$, irrespective of the extractant, and is

TABLE 2.—SOLVATION NUMBERS OF METAL NITRATES IN ORGANIC EXTRACTANTS

Uranyl nitrate extractant	Solvation numbers n', n'' and n''' (See text)		
	n' (using pure solvent)	n'' (from mole fractions)	n''' (from activities)
TBP	2·0	2·0	2·0
DBPP	2·2	2·2	2·0
DPBP	3·2	3·0	
TPP	—	3·0	
DBC	1·6–2·2	3·0	2·0
MIK	3·6–5·1	4·0	
Cobalt nitrate extractant			
TBP	2·4–3·4	4·1	3·0
Sodium nitrate extractant			
TBP	—	3·0	3·0

TABLE 3.—THERMODYNAMIC DATA

Uranyl nitrate extraction from water

Extractant	TBP	DBPP	DPBP	DBC	MIK
$K = \frac{m_{org}}{(m\gamma)^3}$	2230	170	11·3	1·54	0·76
$\Delta G = -RT \ln K$ (cal mole^{-1})	−4580	−3058			
ΔH (cal mole^{-1})	−3615	−4030			
ΔS (cal mole^{-1} °C^{-1})	3·24	−3·26			

Cobalt nitrate extraction from water

Extractant	TBP	DBPP
$K = \frac{m_{org}}{(m\gamma)^3}$	0·170	0·000412
ΔG	1060	4640
ΔH	−8980	−5155
ΔS	−33·7	−32·9

the same as the order of complex stability for all ligands in which oxygen atoms are the only donors. For the extractants, the relative extraction sequence is TBP > DBPP > DPBP > TPP which shows the expected progressive decrease in extraction as the butyl groups in tri-butyl phosphate are replaced by the more electronegative phenyl groups (cf. Part I). It should, however, be emphasized that a number of these solvates are hydrated (see below), and the relative order of partition coefficients obtained as well as their individual magnitudes is governed by this factor as well as by the nature of the phosphoryl group substituents and the solvated metal.

The change in heat content (ΔH) varies from salt to salt but bears no constant relation to ΔG, a heat effect of the same order being obtained whether K is decreased by changing either the extractant or the salt. There is a more positive entropy change when extracting uranyl nitrate than when extracting cobaltous nitrate both with TBP and DBPP. This is evidently due to different solvated species being involved and to the liberation of more water of hydration in the solvation of uranyl nitrate. From analyses of the water and uranium contents of the extracting phases using undiluted extractants, the number of water molecules that appear on the average to accompany uranyl nitrate into TBP is 0, into DBPP is 0·5, into DPBP is 1. Similar approximate figures for cobaltous and sodium nitrates in TBP are $3H_2O$ in each case. KATZIN and FERRARO[7] have shown that if one takes the two nitrates, cobaltous nitrate dihydrate and uranyl nitrate dihydrate and compares their heats of solution in various solvents, the difference is fairly constant at ~6 kcal mole^{-1}. This, they explain, is due to the similarity in type of solute i.e. $UO_2(NO_3)_2 \cdot 2H_2O \cdot 2S$ and $Co(NO_3)_2 \cdot 2H_2O \cdot 2S$. The heats of solution of the dihydrates in TBP are given by KATZIN as −10·46 and −4·74 kcal mole^{-1}. This contrasts with our values of −3·6 and −9·0 kcal mole^{-1} for the change in heat content on extracting $UO_2(NO_3)_2$ and $Co(NO_3)_2$ from an aqueous into a TBP phase. However, as the complexes extracted differ considerably in water and TBP content ($UO_2(NO_3)_2 \cdot 2TBP$ and $Co(NO_3)_2 3H_2O \cdot 3TBP$) the absolute total binding energies of the constituents in these complexes are not easily compared, though entropy changes are evidently of considerable significance in determining their relative extractabilities.

Partition with extractants in inert diluents

Partition data for uranyl, cobaltous and sodium nitrates between water and the phosphate esters to which inert organic diluents were added have been obtained at 25°C and are recorded in Figs. 2–6. Similar data for DBC and MIK in carbon tetrachloride are also recorded (Figs. 5 and 6). The systems and their dilution ranges in mole fractions are given in Table 4. An approximate estimate of the solvation numbers is obtained from the data as follows. Substitution of mole fractions (X) as an approximation for activities of solvent (S) and salt (m_{org}) in equation (2) gives:

$$\frac{m^3\gamma^3 \cdot X_S^{n''-1}}{X_{org}} = \text{constant} \qquad (3)$$

where X_{org} is the mole fraction of salt in the organic solvent. A double log plot of X_S against X_{org} at constant aqueous activity gives a line of slope $(n'' - 1)$. The solvation numbers (n'') obtained in this way are given in Table 2.

More accurate solvation numbers may be obtained from partition data with

[7] L. I. KATZIN and J. R. FERRARO, *J. Amer. Chem. Soc.* **74**, 6040 (1952).

TABLE 4.—DILUTION DATA AND A CONSTANTS IN GIBBS–DUHEM EQUATION (4)

System	Mole fraction of extractant	Constant A
H_2O–$UO_2(NO_3)_2$–TBP–CCl_4	0·567–0·0095	−0·385
H_2O–$UO_2(NO_3)_2$–TBP–C_6H_6	0·328–0·0105	−0·543
H_2O–$UO_2(NO_3)_2$–DBPP–CCl_4	0·460–0·0178	−0·0783
H_2O–$UO_2(NO_3)_2$–DPBP–CCl_4	0·345–0·039	—
H_2O–$UO_2(NO_3)_2$–TPP–CCl_4	0·256–0·029	—
H_2O–$UO_2(NO_3)_2$–DBC–CCl_4	0·638–0·266	−0·85
H_2O–$UO_2(NO_3)_2$–MIK–CCl_4	0·860–0·272	—
H_2O–$Co(NO_3)_2$–TBP–CCl_4	0·692–0·0185	−0·385
H_2O–$NaNO_3$–TBP–C_6H_6	0·328–0·0070	−0·543

diluted extractants by incorporating activities calculated from vapour-pressure measurements, (Table 5).

The values of the activity of the diluent (a_1) in the extractant-diluent system were found to conform with the expression for regular solutions,

$$a_1 = \frac{p_1}{p_1^0} = \frac{n_1}{n_1 + n_2} e^A \left(\frac{n_2}{n_1 + n_2} \right)^2 \tag{4}$$

From the Gibbs–Duhem equation the activity of the non-volatile extractant (a_2) is given by

$$a_2 = \frac{n_2}{n_1 + n_2} e^A \left(\frac{n_1}{n_1 + n_2} \right)^2 \tag{5}$$

Values of the constant A obtained experimentally for TBP, DBPP and DBC in the diluents benzene and carbon tetrachloride are included in Table 4 above. At constant aqueous activity equation (2) may be rewritten as

$$a_S^{n'''} = K'' X_U \tag{6}$$

where a is the activity of the organic solvent (obtained from the vapour-pressure measurements) and X_U is the true mole fraction of the nitrate in the organic phase as defined by

$$X_U = \frac{m_{org}}{m_{solvent} + m_{CCl_4} + (1 - n''')m_{org}.} \tag{7}$$

The value of n is then obtained by plotting $\log a_S$ against $\log X_U$ for different values of n'''. When the correct value of n''' is used, a straight line of slope n''' is obtained over the whole range of solvent/diluent ratios. Solvation numbers (n''') have been obtained for uranyl nitrate in carbon tetrachloride solutions of DBC and DBPP. Values have also been found for the three nitrates with TBP in the same diluent, and for uranyl nitrate in a benzene solution of TBP. In the case of cobalt and sodium nitrates the whole range of solvent activity data could be used, but with uranyl nitrate deviation from linearity was observed at activity (a_S) greater than 0·5 with carbon tetrachloride, and greater than 0·1 with benzene. By using the linear portions only, the variation in water content of the organic phase can be neglected. Apart

Table 5.—Vapour-pressure of extractant/diluent systems at 25·0°C

TBP/C_6H_6 (anhydrous)						
X^*_{TBP}	0·301	0·398	0·483	0·579	0·622	0·690
P/P_0	0·611	0·504	0·402	0·326	0·240	0·221

TBP/C_6H_6 (water saturated)—corrected for vapour-pressure of H_2O								
X_{TBP}	0·272	0·400	0·474	0·567	0·632	0·700	0·745	0·813
P/P_0	0·691	0·554	0·481	0·373	0·308	0·258	0·199	0·145

TBP/CCl_4 (anhydrous)					
X_{TBP}	0·326	0·491	0·595	0·716	0·811
P/P_0	0·591	0·365	0·250	0·174	0·128

TBP/CCl_4 (water saturated)—corrected for vapour-pressure of H_2O									
X_{TBP}	0·262	0·408	0·452	0·519	0·588	0·663	0·718	0·771	0·932
P/P_0	0·715	0·566	0·503	0·434	0·356	0·301	0·244	0·186	0·067

TBP/CCl_4/$UO_2(NO_3)_2$ (water saturated)—corrected for vapour-pressure of H_2O			
X_{TBP}	0·440	0·449	0·835
P/P_0	0·557	0·518	0·137

DBPP/CCl_4 (water saturated)—corrected for vapour-pressure of H_2O						
X_{DBPP}	0·344	0·348	0·481	0·485	0·486	0·679
P/P_0	0·667	0·664	0·546	0·530	0·513	0·309

DBC/CCl_4 (anhydrous)								
X_{DBC}	0·295	0·355	0·461	0·517	0·564	0·619	0·756	0·825
P/P_0	0·661	0·595	0·462	0·386	0·324	0·288	0·161	0·110

DBC/CCl_4 (water saturated)—corrected for vapour-pressure of H_2O		
X_{DBC}	0·447	0·615
P/P_0	0·458	0·290

* The value P is the corrected value for the dry extractant/diluent system, P_0 being the pressure of the pure diluent at 25·0°C. X_{TBP} is the mole fraction of TBP in the extractant/diluent system.

from this neglect of the water content of the organic phase, the only approximation is that the activity coefficient of the solvated nitrate in the organic phase is constant; this assumption should be valid as the data only refer to the linear parts of the plots.

In Table 2 the solvation numbers (n''') obtained by this treatment are compared with those (n') obtained with the same extractants using equation (2) and those obtained (n'') with diluted extractants using equation (5). The latter are in a number of instances higher than n''' and n'. In general there is good agreement between n''' and n', which suggests that the species present in the organic phase are $UO_2(NO_3)_2 \cdot 2S$, $Co(NO_3)_2 \cdot 3S$ and $NaNO_3 \cdot 3S$ where S is TBP and may also be DBPP and DBC in the case of uranyl nitrate. The value of 3 for n' and n'' obtained with DPBP and TPP indicates that the solvated species in these instances is $UO_2(NO_3)_2 \cdot 3S$. In addition, as already stated, water molecules are present in a number of the solvates. While structures have been postulated[1] for the anhydrous solvates $UO_2(NO_3)_2 \cdot 2S$, it is difficult to assign structures to the hydrated solvates discussed here, as it cannot be stated whether the extractant is bound directly to the uranium, or by hydrogen bonding to a metal-associated water molecule. Neither can it be assumed that the nitrates behave as bidentate or monodentate ligands in the solvated complex.

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OBSERVATIONS ON THE RARE EARTHS—LXIX*

AN ELECTROCHEMICAL INVESTIGATION OF ETHYLENEDIAMINE SOLUTIONS OF LANTHANUM NITRATE

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(*Received* 27 *October* 1958)

Abstract—The solubility of anhydrous lanthanum nitrate in ethylenediamine is markedly dependent upon the water content of the latter. Conductance data for both completely anhydrous solutions and those containing controlled quantities of water show generalized weak electrolyte behaviour. Electrolyses of such solutions yield cathode deposits that apparently contain small quantities of elemental lanthanum. X-ray characterization of such deposits is negated by oxide absorption of radiation diffracted by the metal. Some of the techniques essential to handling materials under anhydrous conditions are described.

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IN earlier reports from this laboratory,[1-3] the electro-chemical characteristics of ethylenediamine solutions of certain anhydrous rare-earth metal and thorium compounds have been described. Although conductance data indicated generalized weak electrolyte behaviour in all cases, the cathodic deposition of at least small quantities of yttrium, neodymium, and lanthanum was suggested by data obtained for electrolyses. Of the more ionic rare-earth metal compounds investigated, however, only lanthanum nitrate and neodymium iodide were sufficiently soluble to be potentially useful.[1] Methods of synthesis then available did not yield products of sufficient purity for conclusive study, but the development of a convenient technique for the preparation of anhydrous nitrates[4,5] has made this class of compounds available. To this end, lanthanum nitrate has been investigated as both the most ionic and least readily reducible of the rare-earth metal nitrates. Choice of this compound has been dictated also by availability of a comparative abundance of X-ray diffraction data for lanthanum metal and its compounds. It is reasonable to extrapolate the data presented for this system to those containing other anhydrous rare-earth metal nitrates with due allowance for decreases in basicity and ionic character from lanthanum to the higher members of the series.

EXPERIMENTAL

Materials and apparatus. Commercially available ethylenediamine was purified by a modification[1,3] of the procedure of PUTNAM and KOBE.[6] The freshly distilled product had a specific conductance of $0{\cdot}46 \times 10^{-6}$ mho cm^{-1} at 30°C, but moisture contamination during storage and handling in the dry box raised this to $0{\cdot}79$–$1{\cdot}36 \times 10^{-6}$ mho cm^{-1}.

* For part LXVIII, see T. MOELLER, E. GULYAS and R. H. MARSHALL, *J. Inorg. Nucl. Chem.* **9**, 82 (1959).

[1] T. MOELLER and P. A. ZIMMERMAN, *J. Amer. Chem. Soc.* **75**, 3940 (1953).
[2] T. MOELLER and P. A. ZIMMERMAN, *Science* **120**, 539 (1954).
[3] T. MOELLER and T. MUNIYAPPAN, *J. Inorg. Nucl. Chem.* **4**, 216 (1957).
[4] T. MOELLER and V. D. AFTANDILIAN, *J. Amer. Chem. Soc.* **76**, 5249 (1954).
[5] T. MOELLER, V. D. AFTANDILIAN and G. W. CULLEN, *Inorganic Syntheses* Vol. 5, p. 37. Wiley, New York (1957).
[6] G. L. PUTNAM and K. A. KOBE, *Trans. Electrochem. Soc.* **74**, 609 (1938).

Freshly ignited 99·9+ per cent lanthanum oxide* was converted to the anhydrous nitrate by treatment with nitrogen(IV) oxide.[4,5] The product was stored in a glass container provided with the "inner" fitting of a standard-taper joint, the "outer" fitting being so sealed as to act as a cap. Grease used to render the container gas-tight thus could not contaminate the anhydrous salt during transfer operations.

Manipulation.[7] All anhydrous materials were handled in carbon dioxide-free air in a "Gloved Box, Berkeley Type", Model R1104, supplied by Radioisotope Applications Company, Albany, California. The circulating atmosphere was passed continuously over soda lime (previously dried at 110°C), 8-mesh activated alumina, and phosphorus(V) oxide. The last of these was renewed every two days; the other two at least every week.

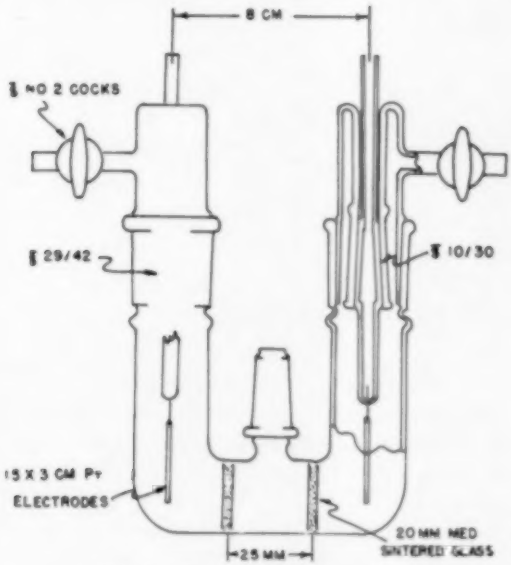

FIG. 1.—Compartmented electrolysis cell.

Solubility determinations. The procedure followed was essentially that previously outlined,[8] except that equilibration at 30 ± 0·025°C was for four days. The tubes were then centrifuged for 30 min at 5000 rev/min, returned to the constant-temperature bath for 30 min and finally removed to the dry box where separation of the supernatant solution from undissolved solid was effected by immediate pipetting. Analysis was carried out by addition of excess water to an aliquot, removal of the precipitated hydrous hydroxide, and ultimate ignition to weighable oxide.

Conductance measurements. Conductance values were obtained at 30 ± 0·025°C as previously described[8] and with the same bridge. Cells used all had bright platinum electrodes, with cell constants 0·111, 0·445 and 0·745 cm^{-1}. All values were corrected for the conductance of the solvent.

Electrolyses experiments. Electrolyses were carried out in the compartmented cell shown diagrammatically in Fig. 1. Use of two barriers effectively eliminated diffusion of anode products into the catholyte. Electrodes used were bright platinum. Current was supplied from a vacuum-tube rectifier with an output voltage variable between 1 and 300 V. Gases released were either trapped for analysis in a Burrell apparatus or allowed to escape through oil traps. Electrolysis was always effected at

* From the Lindsay Chemical Division, American Potash and Chemical Company, West Chicago, Illinois.

[7] G. W. CULLEN, Thesis, University of Illinois (1956). Complete details on manipulative techniques under anhydrous conditions appear in this reference.

constant total current and was terminated when the potential drop across the cell rose to 300 V. The cell was filled in the dry box, but electrolysis was carried out outside the dry box. Cooling during electrolysis was done by a water or ice bath. At the termination of an electrolysis, the cell was returned to the dry box and the cathode removed. Solvent was evaporated from the cathode deposit. One portion of the latter was sealed in a Lindemann capillary for X-ray examination;† a second was heated above 800°C in a Vycor tube, first *in vacuo* and then in argon, to agglomerate the product. This material was examined microscopically and by X-ray diffraction.

X-ray diffraction. Measurements were made with a Hayes 7 cm (radius) camera, using both copper (40 kV, 15 mA, nickel foil filter) and molybdenum (40 kV, 20 mA, zirconia filter) radiation. The former gave better defined and well spread-out patterns. A 0·01 cm pinhole was employed with a specially constructed collimator to aid in positioning the sample.[7]

Microphotography. A Zeiss Ultraphot was used. The sample was contained in the protected lucite holder indicated in Fig. 2.

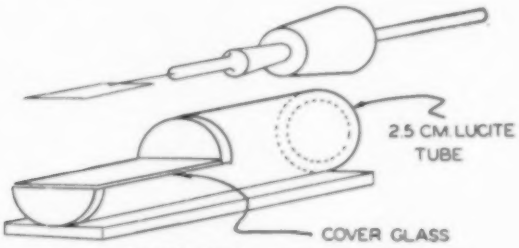

FIG. 2.—Cathode container for microphotography.

RESULTS AND DISCUSSION

Solubility. The solubility of anhydrous lanthanum nitrate is closely dependent upon trace quantities of water in ethylenediamine. The ease with which the latter absorbs moisture thus renders the results quite variable. The smallest value obtained

TABLE 1.—SOLUBILITY OF LANTHANUM NITRATE IN ETHYLENEDIAMINE AT 30°C AS A FUNCTION OF WATER CONTENT

Water content (% by weight)	Solubility $La(NO_3)_3$ (g/l.)
0·00	4·66
0·191	15·41
0·287	21·10
0·383	23·63
0·479	20·15
0·574	15·04
0·670	5·84

for freshly distilled solvent was 3·81 g/l. at 30°C; the largest, 5·88 g/l. The saturated solution used for dilution in conductance studies contained 4·66 g/l. Solubility was determined as a function of added water, using 50 ml volumes of solution containing measured quantities of water. The data, as summarized in Table 1, suggest that the

† This is done conveniently in the dry box by supporting the sealed end of the capillary in a nest of glass wool, dipping the open end into the sample, and tapping gently to settle the solids. The tube is sealed temporarily with "Plasticene" and then permanently by flaming after removal from the dry box.

24·5 g/kg of solvent previously reported[1] resulted from the presence of considerable moisture. Decrease in solubility above ca. 0·4 per cent water appears to be due to hydrous hydroxide separation as a result of reaction between water and ethylenediamine.

Anhydrous lanthanum nitrate dissolves in anhydrous ethylenediamine to a clear, colourless solution. Since very little heat is evolved in the process, the energy of solvation is low. However, if a trace (or more) of water is present, considerable heat is evolved with hissing and sputtering as the solute contacts the liquid. If the solute is added rapidly, the solvent may burst into flame. In any event, the resulting solution is pale yellow. Energy released in hydration is sufficient to promote oxidation of ethylenediamine by nitrate ion.

TABLE 2.—CONDUCTANCE DATA FOR LANTHANUM NITRATE SOLUTIONS AT 30°C

Concentration N (equiv/l.)	$\sqrt{N} \times 10$	Equivalent conductance (mho cm² equiv⁻¹)		
		0·00% H_2O	0·191% H_2O	0·383% H_2O
0·2000	4·47			10·77
0·1500	3·87			10·85
0·1000	3·16		10·70	11·60
0·0800	2·83		11·50	12·25
0·0600	2·45	7·75	12·00	13·50
0·0400	2·00	9·45	13·25	15·80
0·0200	1·41	13·70	17·80	20·10
0·0100	1·00	20·00	24·00	24·25
0·0080	0·89	22·15	26·60	25·75
0·0060	0·77	25·15	28·60	27·90
0·0040	0·63	31·00	32·50	31·50
0·0020	0·45	42·15	42·15	
0·0010	0·32	53·75	53·50	
0·0008	0·28	58·60		
0·0006	0·25	63·75		
0·0004	0·20	74·15		
0·0002	0·14	95·00		

Conductance studies. Conductance data for both anhydrous systems and those containing controlled quantities of water are summarized in Table 2 as values interpolated at rounded concentrations from appropriate phoreograms.[8] The indicated behaviour is that of a weak electrolyte under all conditions studied. This is in agreement with data obtained for other tripositive rare-earth metal compounds in ethylenediamine[1,9] and is that expected for a compound of a highly charged cation in a solvent of moderate dielectric constant (12·8 at 25°C) where ion-pair formation is sizable.[3] Improvement in conductance at a given concentration as water is added is probably due to the formation of a more mobile $La(H_2O)_n^{3+}$.

[8] R. M. FUOSS, *J. Chem. Educ.* **32**, 527 (1955).
[9] T. MUNIYAPPAN and B. ANJANEYALU, *Proc. Indian Acad. Sci.* **45**, 412 (1957).

Electrodeposition studies. Both cathodic evolution of gases and the formation of adherent cathode deposits characterized electrolyses in either anhydrous ethylenediamine or ethylenediamine containing less than 0·4 per cent water. In a typical electrolysis with a saturated solution under anhydrous conditions at a constant current density of 1·1 mA/cm², the applied potential increased from 155 to 300 V in 4 hr with only a slight increase in temperature. The anolyte became yellow, but the solution in the central compartment remained colourless. Gas released at the cathode was ca. 70 per cent hydrogen by volume, the remainder being inert. The dried cathode deposit appeared amorphous and non-metallic (Fig. 3), but only lanthanum oxide could be detected by X-ray diffraction. Heat treatment effected agglomeration and formation of metallic appearing globules (Fig. 4), but again no diffraction lines other than those for lanthanum oxide could be detected. The heat-treated product displaced hydrogen slowly from water and rapidly from acids. Results for other electrolyses were similar. The dried cathode deposits invariably contained carbon, hydrogen, and nitrogen as well as lanthanum, a typical analysis being C, 7·77; H, 2·71; N, 6·78; La, 58·25%. Such data suggest contamination by organic material (solvent or solvent decomposition products) rather than a compound of definite stoicheiometry.

In a typical electrolysis with a saturated solution containing 0·13 per cent water with a current of 30 mA, the potential was increased from 100 to 275 V in 4 hr. In this period ca. 36 per cent of the lanthanum was removed from solution, and a voluminous, light yellow cathode deposit resulted. Heat treatment yielded a light coloured matrix containing dark flakes and shiny, metallic spheres. X-ray diffraction indicated only lanthanum hydroxide in the unheated deposit and lanthanum oxide in the heated. However, the material liberated hydrogen when added to water. Gases evolved at the cathode contained 71 per cent hydrogen, 25 per cent unreactive, and 4 per cent combustible material. Results with solutions containing up to 0·386 per cent water were closely comparable. It is perhaps pertinent that bright, clean lanthanum turnings in contact with ethylenediamine containing ca. 0·38 per cent water turned black but did not dissolve.

The data, suggest, but do not prove conclusively, the presence of elemental lanthanum in the cathode deposits. The best supporting evidence is from microscopic and chemical observations. Failure of the X-ray diffraction technique may be due to absorption of the diffracted rays from small particles of metal by oxide layers surrounding them. Thus, it was shown that a thin layer of lanthanum oxide interposed between a sample of lanthanum metal and the photographic film in the diffraction camera obliterates almost completely the characteristic pattern of the metal. The marked similarity among the patterns of lanthanum, lanthanum oxide, and lanthanum hydroxide[7] is a further source of difficulty in this method of characterization.

That sizable deposits of lanthanum did not result under the conditions employed does not preclude the deposition of other less active rare earth metals, but it does suggest that their deposition in quantity is unlikely. The results reported illustrate still further BRENNER's contention[10] that ionic character in a salt, the use of a solvent of reasonable dielectric constant, and electrodeposition of a metal are not always related.

Acknowledgement—The authors are indebted to the Air Force Office of Scientific Research for the financial support which rendered this study possible. The work was done under Contract AF 18(600)-1535.

[10] A. BRENNER, *J. Electrochem. Soc.* **103**, 652 (1956).

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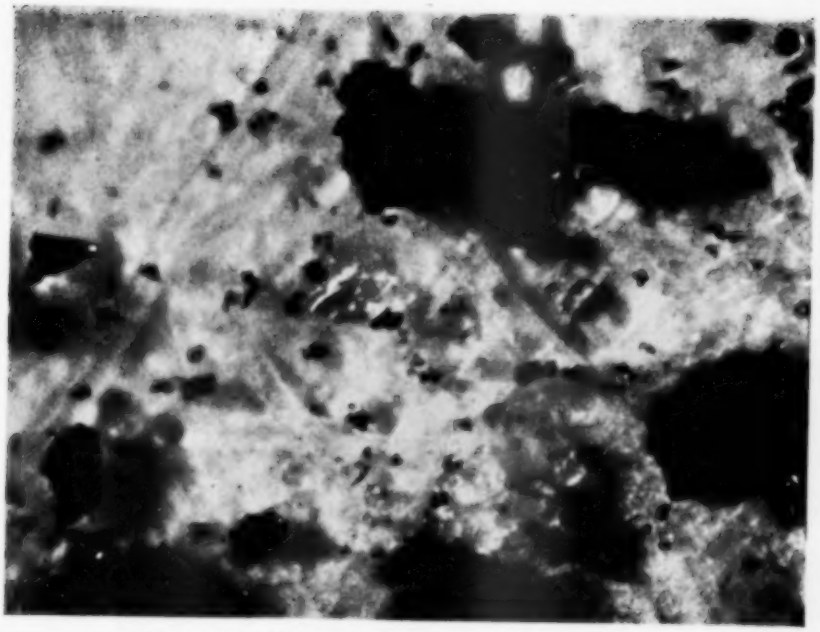

FIG. 3.—Microphotograph of untreated cathode deposit. ×100.

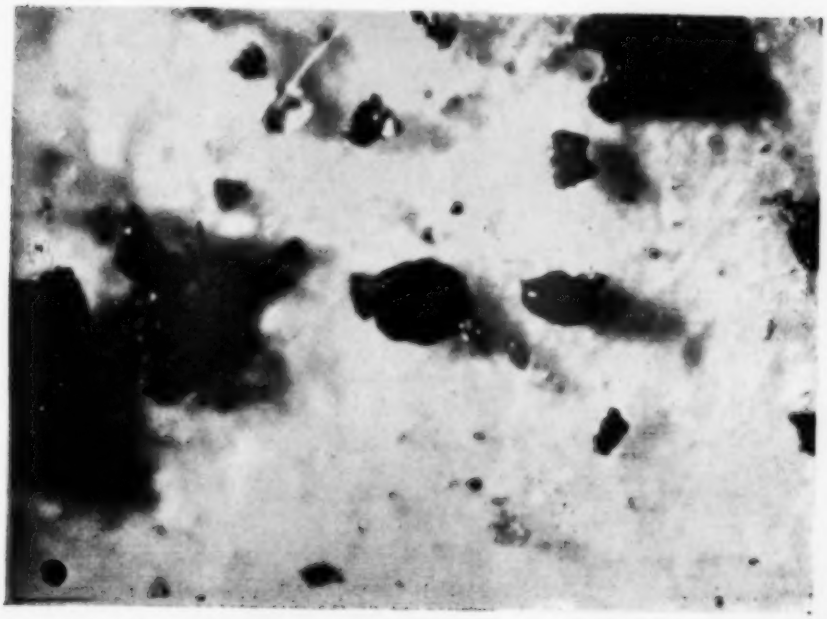

FIG. 4.—Microphotograph of heat-treated cathode deposit. ×100.

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AN APPARATUS FOR THERMOGRAVIMETRY IN HAZARDOUS ATMOSPHERES

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Eldorado Mining and Refining Limited, Ottawa

(*Received* 15 *June* 1958)

Abstract—A detailed description is given of the construction and operation of an apparatus, incorporating a commercial pen-recording thermobalance, designed for the study of reactions involving hazardous gases. A leak detector for water-soluble gases has been designed especially for use with the assembly.

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INTRODUCTION

THE value of thermogravimetry as an analytical and research technique has become widely recognized since its introduction, but the literature lacks reference to means of carrying out reaction studies in flowing gases where these, or their volatile products, are corrosive and toxic.

Requirements for such an apparatus include the maintenance of a steady symmetrical flow to avoid spurious weight changes and arrangements to prevent escape of gas from the reaction chamber, involving efficient disposal of excess reagent. The model to be described, which is used in conjunction with the Stanton thermobalance,* has been used extensively, without mishap of any kind, for reaction rate investigations in hydrogen fluoride gas and for studies involving uranium and its compounds. The parts subject to attack are constructed of Monel or Inconel alloy. A nitrogen seal separates the reaction zone from the balance, and a leak detector for water-soluble gases is incorporated as a precautionary device.

The standard functions of the thermobalance remain unaffected by this extension of its versatility and the metal tube can easily be replaced by one of silica, using the same seal and exhaust structure.

The general arrangement of the apparatus is shown in Fig. 2.

CONSTRUCTION AND OPERATION

1. *Structural modifications to the Stanton thermobalance*

The apparatus requires very little alteration to the thermobalance as supplied. The four vertical rods (Fig. 1) carrying the tube furnace and transformer may be extended by 4 in. if frequent interchange of metal and silica reaction tubes is envisaged. This allows removal of the metal reaction chamber from the lower end of the furnace. The uppermost heat shield plate over the balance case has been dispensed with.

The main modification is to the silica furnace liner carrying the nichrome winding. Since this winding must not contact the metal tube, the pin at its lower end is recessed by drilling the tube to about one-third of its thickness with an abrasive tool, the depression being filled with refractory cement. The projecting winding at the upper end is also insulated with cement.

* Supplied by Stanton Instruments Limited, 119 Oxford Street, London.

2. *Gas control system*

Plastic or copper tubing, and brass needle valves may be used for gases other than those of a corrosive nature, where either Monel or Inconel are employed. Correct metering of hydrogen fluoride requires that its temperature should be kept above 80°C and the tubing which carries it is heated by turns of insulated resistance wire and

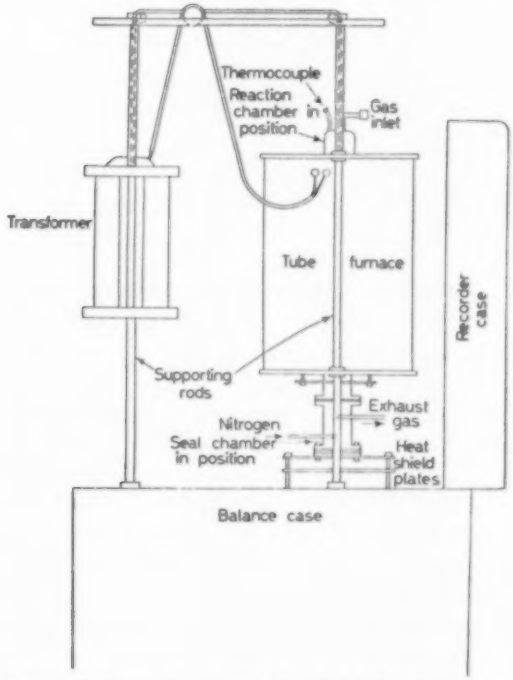


FIG. 1.—Plan of thermobalance with reaction chamber and seal compartment in position.

lagged with asbestos string. A thermocouple or thermometer is inserted between the tube and wire to ensure that a suitable temperature (about 150°C) is achieved.

Flow-meter *A* (Fig. 2) measures the nitrogen flow to the seal compartment. *B* carries nitrogen or argon for purging the apparatus or for diluting another gas, such as hydrogen, to be introduced through *C*. *D* is an illuminated polytetrafluorethylene flow-meter for hydrogen fluoride or other corrosive gas. *E* is reserved for air or oxygen and is detached from the reaction chamber inlet line when the rest of the system is in use, to avoid accidentally forming an explosive mixture with hydrogen.

3. *The reaction chamber*

This section of the apparatus operates under severe conditions and Inconel appears to have some advantage over Monel as the constructional material. It is 12 in. long, $1\frac{7}{8}$ in. outside diameter and has a wall thickness of 1/32 in. with fittings at its upper end for the attachment of the gas inlet tube and for accommodating an Inconel-sheathed platinum–platinum-rhodium thermocouple: the latter lies along the inside of the reaction chamber with its tip at sample level.

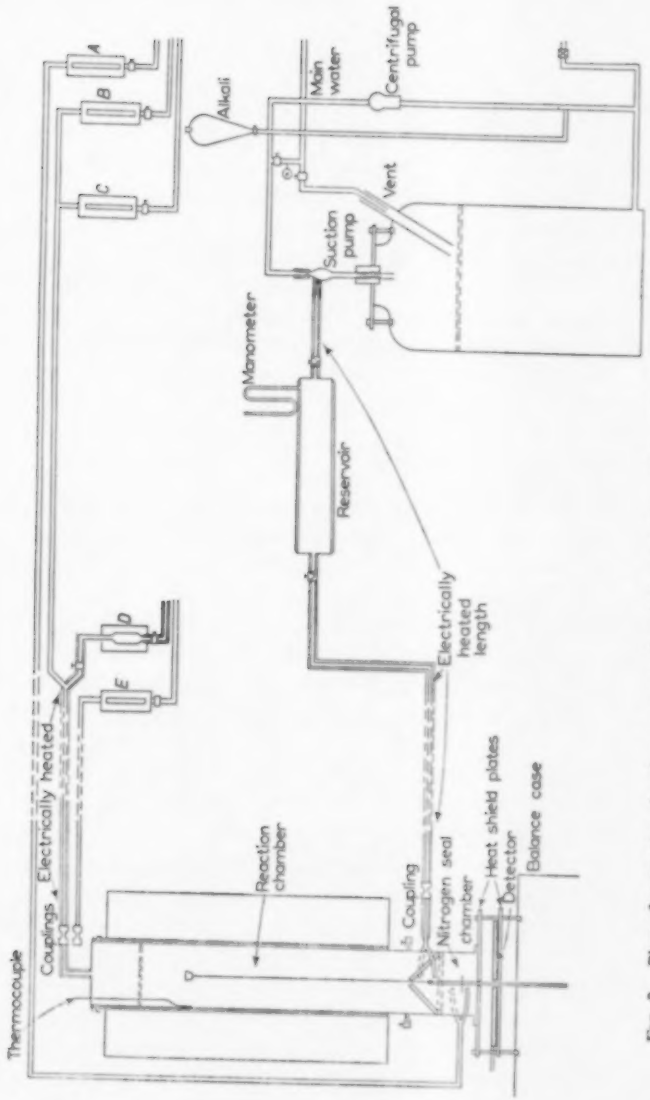


FIG. 2.—Plan of apparatus showing gas control and disposal assemblies, reaction chamber and seal compartment.

At the lower end of the chamber is a $\frac{5}{8}$ in. flange for clamping to the seal compartment: a second detachable flange, provided with set-screws, positions the reaction chamber in the furnace.

An internal perforated plate, welded 3 in. below the upper end, prevents direct impingement of gas on the sample and also serves to promote mixing and heating of the gas.

4. *The seal compartment*

Unlike the reaction chamber, this does not move with the furnace but is fixed to the heat baffle plates at the top of the balance case. Apart from its length, 2 in. its dimensions are those of the reaction chamber, and it also carries flanges for attachment to the balance and for clamping to the reaction chamber. Ring gaskets of polytetrafluorethylene act as heat and gas seals in both positions.

Internally, it is divided into two parts by a hollow metal cone accurately seated by grinding on a support. The rod carrying the sample passes through the axis of this cone, above which waste gases are extracted via two diametrically opposite, $\frac{1}{4}$ in. diameter outlets. Below the cone, the inflow of nitrogen through two similarly placed orifices forms the actual gaseous seal.

5. *The leak detector*

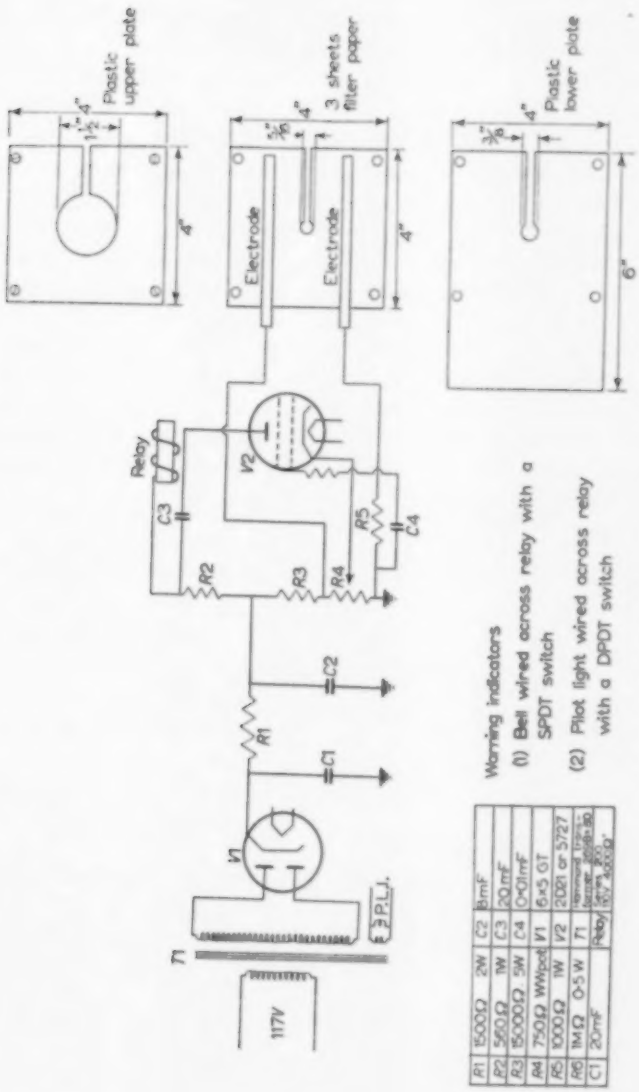
In principle the detector, which is positioned just below the seal compartment with the sample support rod passing through the central hole, consists of two electrodes in contact with filter paper soaked in distilled water. Its sensitivity is set by adjusting a potentiometer until the warning circuit just fails to operate: thereafter, a slight leak of hydrogen fluoride, ammonia or other water-soluble gas leads to an increased conductivity of the medium between the electrodes and audible warning of the event is given. A simple modification using solenoid valves would permit the cut-off of the gas flow to the reaction chamber and the stepping-up of the exhaust rate.

Constructional details of the detector are shown in Fig. 3.

6. *The constant-suction gas absorber*

Waste reactant gases, or gaseous reaction products, are exhausted from the reaction chamber by a laboratory suction pump discharging into a 10 gal polythene bottle and driven by water recirculated through a centrifugal pump delivering a pressure of 40 lb/in^2. In case of necessity water from a main supply may be used, but its pressure, and consequently the suction exerted, is subject to fluctuations. A small flow of water flushes the absorption bottle and discharges to waste through a non-return valve at a level sufficient to keep the bottle about one-third filled. A perforated plate fixed below the suction pump promotes solution of such gases as ammonia and hydrogen fluoride, and volatile fluorides, etc., produced in the reaction under study. Neutral gases such as nitrogen escape through a vent extending almost to the level of the plate: in some instances it may be necessary to extend the vent to a fume hood; for example, if carbon monoxide is used.

To avoid corrosion of the suction pump and sewers, an alkali solution is fed into a transparent plastic section of the centrifugal pump input line. Addition of a small



R1	1500Ω 2W	C2	8mF
R2	560Ω 1W	C3	20 mF
R3	15000Ω 5W	C4	0·01mF
R4	750Ω WWpot	V1	6×5 GT
R5	1000Ω 1W	V2	2D21 or 5727
R6	1MΩ 0·5 W	T1	Primary 200-250V 50c/s 60W Secondary 6·3V 2·5A
C1	20mF	Relay	6K2A 4000Ω

FIG. 3.—Leak detector and warning circuit.

amount of indicator, such as methyl red solution, to the contents of the bottle from time to time gives a visual check on their suitability for discharge.

The extraction line between the suction pump and the reaction chamber is of Monel or Inconel alloy tubing, heated and lagged to prevent condensation along its length. It includes a reservoir of about $1\frac{1}{2}$ gal capacity (this may be constructed of copper or brass) to take up minor irregularities of suction, and also a U-tube manometer. The needle valves at either end of the reservoir are of Monel or Inconel.

The required exhaust rate is set by disconnecting the suction line at a coupling near the reaction chamber and drawing air through a laboratory flow meter via a plastic tube (the needle valves and metal tubing should of course be at operating temperature during calibration). The manometer will then indicate the suction to be maintained in the reservoir throughout the experimental run: its level will change on removal of the flow-meter due to the latter's resistance, and should be returned to its original value by slightly closing the needle valve nearest the reaction chamber, thereby restoring the measured exhaust rate.

The rate of extraction from the reaction chamber is appropriately fixed at a value slightly less than the total of the rates of inflow of reactant and seal gases: thus, there will be a slow discharge of pure nitrogen below the seal compartment preventing both entry of atmospheric oxygen and efflux of corrosive gas and giving a margin of safety in case of surges of reactant or fluctuations in exhaust rate. For example, an exhaust rate of 1·5 l/min is satisfactory with a nitrogen seal flow of 0·75 l/min and a gas input of 1 l/min.

Acknowledgement—B. BURROWS constructed the electronic circuit of the leak detector.

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NOTES

Composition and stability constant of a complex of cerium and ammonium citrate at alkaline pH

(*Received* 16 *October* 1958; *in revised form* 20 *January* 1959)

THE composition and stability constant of a complex of cerium and citrate ion were determined by the ion exchange method.[1,2,3] The adsorbent used was Zeocarb 225, in the NH_4^+ form and 70/100 mesh size.

Portions of 350 mg of the cation exchanger were shaken in a thermostat at 25° ± 0·5°C with 30 ml of solutions in Erlenmeyer flasks; the pH, ionic strength and the concentrations of Ce^{3+} and NH_4^+ were maintained constant. The pH of the solutions was adjusted to 8·0 by the addition of 1N $HClO_4$. The concentrations of citrate used are recorded in Table 1. The isotope used was carrier free ^{144}Ce in tracer concentration and the determination of the activities were made in a Geiger counter for liquids, type M6C.

After 24 hr 10 ml of the solution were removed and the activity measured. The amount of Ce bound to the exchanger was not determined by difference since previous experiments showed that the amount adsorbed on the walls of the flasks caused considerable errors. Under these conditions, the exchanger was separated from the solution, washed rapidly and shaken for 48 hr with 30 ml of concentrated ammonium citrate solution at pH 8·0.

Having seen from previous experiments that, under these conditions, one could get a practically complete recovery of the cerium bound to the exchanger, the activity of the latter was thus determined from 10 ml of that solution, which practically eliminates the errors due to absorption by the walls of the flask.

As is already known, the equilibrium between a metal ion in solution and the same ion bound to a cation exchanger may be expressed in terms of the distribution coefficient

$$\alpha_0 = \frac{RM}{[M]} \qquad \text{(a)}$$

where RM is the number of moles of the metal bound per unit weight of the cation exchanger and $[M]$ the concentration of the metal ion in solution at equilibrium. In the presence of a complexing agent there is the additional equilibrium

$$M + {}_n\text{Cit} \rightleftharpoons (\text{Cit})_n M, \quad \text{and} \quad K_d = \frac{[(\text{Cit})_n M]}{[M]\,[\text{Cit}]^n} \qquad \text{(b)}$$

The distribution coefficient between the cation exchanger and the solution is

$$\alpha = \frac{RM}{[M] + [(\text{Cit})_n M]}$$

(1) J. SCHUBERT, *J. Phys. Coll. Chem.* **52**, 340 (1948).
(2) J. SCHUBERT and RICHTER, *J. Phys. Coll. Chem.* **52**, 350 (1948).
(3) J. SCHUBERT and RICHTER, *J. Amer. Chem. Soc.* **70**, 4259 (1948).

or, substituting from (a) and (b),

$$\frac{1}{\alpha} = \frac{1}{\alpha_0}\left(1 + K_d[\text{Cit}]^n\right) \qquad (c)$$

or

$$\log\left(\frac{\alpha_0}{\alpha} - 1\right) = \log K_d + n \log [\text{Cit}] \qquad (d)$$

Thus, log K_d and n may be obtained directly from the intercept and slope of a plot of $\log\left(\frac{\alpha_0}{\alpha} - 1\right)$ versus log [Cit].

From the results obtained for the distribution coefficient α (Table 1) we were not able to determine the distribution coefficient α_0 in the absence of the complexing agent by extrapolation with reasonable accuracy, since values between 2·0 and 3·5 were obtained.

TABLE 1

Conc. in citrate moles/l. × 10^4	Activities* (counts/5 min)		α	$\log(\alpha_0/\alpha - 1)$
	solution	Exchanger		
10·0	5270	258	0·049	1·70
5·62	5046	688	0·136	1·24
3·16	3760	1494	0·397	0·72
2·37	3135	1691	0·540	0·56
1·78	2537	2612	1·03	0·176
1·33	2194	2810	1·28	−0·021

* Counts were repeated until a statistical error of less than 1·5% was obtained.

However, when substituting those values in equation (d) straight lines with slopes (values of n) between 1·9 and 2·2 are obtained. Under these conditions we accepted as the most probable value $n = 2$, attributing to the complex the formula $(\text{Cit})_2\text{Ce}^{---}$.

Since n is now known, it is clear from equation (c) that a straight line is obtained by plotting $(1/\alpha)$ vs. $[\text{Cit}]^2$ which enables us to determine α_0 by extrapolation more accurately (Fig. 1).

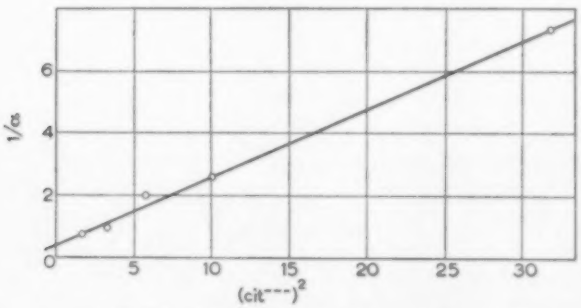

FIG. 1.—Determination of α_0 by extrapolation.

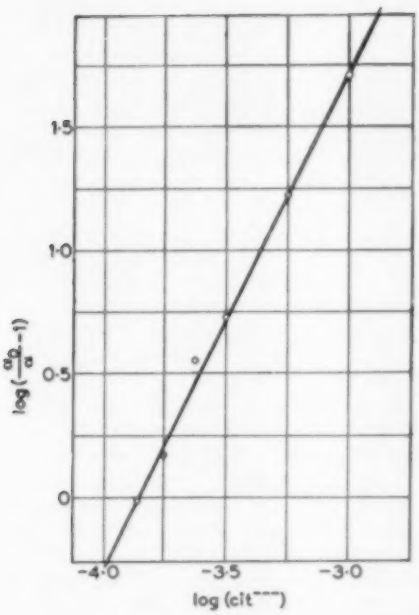

FIG. 2.—Determination of stability constant.

Considering $\alpha_0 = 2{\cdot}5$ according to Fig. 1, we have $K_d = 5{\cdot}3 \times 10^7$ for the formation constant of the complex at pH = 8·0, found by a graphical plot of equation (d), shown in Fig. 2.

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Separation of gadolinium from ^{235}U fission product rare earths

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THE fission process of natural uranium leads, among the 200 radioactive species, to varying yields of 52 different isotopes of rare earths ranging from lanthanum to terbium. The chemical behaviour of these elements enables a separation of a mixed fraction of all the rare earths from the other fission products, but makes it difficult to separate these elements from each other.

In the present paper a procedure is described for the separation of micro quantities of gadolinium from other natural uranium fission product rare earths. The literature already contains separation procedures for all these elements, though often of rather limited scope, because the main aim has been to separate the major rare earth constituents of ^{235}U fission. So far no procedure has been proposed

for the separation of the minor constituents gadolinium and terbium. Our work extends the information available by the application of paper electrophoresis techniques for the separation of fission product rare earths.

The apparatus used was similar to that described previously[1] and consisted of two flat glass plates and two beakers with the electrolyte. Whatman No. 1 paper sheet was stretched horizontally and enclosed by the glass plates with the ends dipping into the carrier electrolyte. The paper was first wetted with the electrolyte by dipping, then blotted with the same paper and, starting at the anode end, about 20–50 μl of the solution containing the rare earths was applied from a micropipette along a length of about 4 cm and across the whole width of the paper. The paper was then placed in position in the apparatus and 400 V potential applied for a minimum of 2 hr through two platinum electrodes immersed in the beakers. The current carried by the moist paper strips was approximately 3–4 mA. No heating of the covered strips was observed. Finally, the electrodes were removed, the sheets air dried, and the spots made visible by spraying with alcoholic ammoniacal 8-quinolinol. Fluorescent spots appeared in ultra-violet light. Radioisotopes were detected by their β–γ activities using either a Victoreen 1 B 85 thyrode counter tube with thin metal wall or a Nuclear Instrument, model D 34, mica end-window tube.

The separation of the rare earths by paper electrophoresis was tried using aqueous solutions of sodium thiosulphate, potassium iodide, potassium chromate, potassium bromate, phosphoric, citric, tartaric, gallic, succinic, malonic and thioglycolic acids in various concentrations as electrolytes. Only the thioglycolic acid showed some possibilities for an electrophoretic separation in the group of the rare earth elements. In addition to the separation of gadolinium from other rare earths described in this paper, it was possible to separate yttrium and zirconium from the lanthanons and thorium. These results will be published later.

The background electrolytic solution was prepared by dissolving analytical grade Eastman Organic Chemical (white label) product thioglycolic (mercaptoacetic) acid in water to give a 25 per cent solution. Lower concentrations of the acid were also tested, but the above concentration was found to be necessary and sufficient in order to obtain compact zones. The mixture of ions submitted to electrical migration was prepared from the nitrates, being either BDH or Baker & Adamson, New York, products. Solutions of radioisotopes of ^{144}Ce, ^{154}Eu, ^{153}Gd and ^{147}Pm, made up in dilute nitric acid, were obtained from A.E.R.E., Harwell.

The rare earth isotopes represent about 25 per cent of the slow-neutron ^{235}U fission products, calculated from the cumulative yields of the mass numbers. This amount is somewhat lower in the first 2 weeks after irradiation is stopped, owing to the mass number 140 (stable cerium being formed by the decay of barium with a half-life of 12·8 days). After this period, although there is no further change in the absolute amounts of total rare earths, the relative composition of the rare earth mixture in fission products depends on the cooling time. These changes are due to decays in mass numbers 141 (half-life 32 days), 143 (13·7 days) and 144 (285 days). All other rare earth isotopes formed after a period of 2 weeks are either stable or long-lived (over a year) isotopes. The approximate relative percentage composition of a fission product rare earths mixture at various times after the irradiation is given in Table 1. The table has been compiled on the basis of published data[2] for the percentage values of the elements representing the cumulative fission yield values for the mass numbers. As seen from the table, gadolinium represents practically the smallest component in fission-product rare-earths mixture, with a total of 0·05 per cent all of them stable isotopes.

In a typical fission product starting solution in nitric acid the total concentration of the rare earths is approximately 0·08 g/l.[3] The concentration of the total rare earths in the artificial mixtures prepared in this study was 0·8 g/l. or 2·5 g/l., as $RE(NO_3)_3 \cdot 6H_2O$ in 1 M nitric acid, this being the minimum necessary for their detection by the quinolinol reagent. Four artificial mixtures were prepared according to the percentage composition shown in Table 1. To the above mixtures marked

[1] M. Lederer and F. L. Ward, *Austr. J. Sci.* **13**, 114 (1951); S. Kertes and M. Lederer, *Anal. Chim. Acta* **16**, 40 (1957).

[2] E. P. Steinberg and L. E. Glendenin, *Proceedings of the First International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Paper No. P/614, United Nations, New York (1956); H. Götte and D. Pätze, *Angew. Chem.* **69**, 608 (1957); I. Prawitz and I. Rydberg, *Acta Chem. Scand.* **12**, 369, 377 (1958).

[3] T. V. Healy, P. E. Carter and P. E. Brown, *Process Chemistry* Vol. I, p. 363. Pergamon Press, London (1956); I. M. Fletcher, *Ibid.* p. 105.

TABLE 1.—THE APPROXIMATE RELATIVE COMPOSITION OF A FISSION PRODUCT RARE-EARTH MIXTURE AFTER VARIOUS COOLING TIMES*

Rare earths	Cooling time			
	1 day (%)	14 days (%)	30 days (%)	1 year (%)
La	13·2	11·6	11·6	11·6
Ce	53·7	47·7	40·9	23·9
Pr	—	12·0	—	—
Nd	27·8	19·4	31·4	42·2
Pm	4·0	5·0	11·8	18·0
Sm	1·2	3·9	3·9	3·9
Eu	0·1	0·35	0·35	0·35
Gd	0·03	0·05	0·05	0·05
Tb	0·002	0·002	0·002	0·002

* Compiled from data in Ref. (2).

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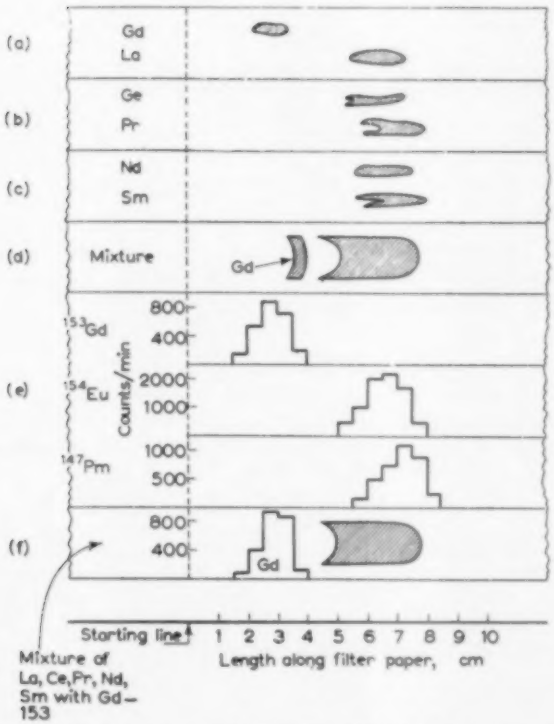

FIG. 1.—Electrophoretic migration of rare earths. Migration of macro-amounts of individual rare earths (a–c); migration of tracer amounts of ^{153}Gd, ^{154}Eu and ^{147}Pm (e); electrophoretic separation of macro amounts of La, Ce, Pr, Nd and Sm from macro amounts (d) and tracer amounts (f) of Gd. Concentrations of tracers are represented by count profiles, and areas of macro quantities by shaded areas.

europium and gadolinium nitrate were added because their low concentration did not allow chemical detection on paper. The results are shown in Fig. 1: sections (a–c) show the migration of 1·5 mg of the individual rare earths; (d) represents the separation of 1·5 mg of gadolinium from the other five major constituents in a mixture containing equi-amounts of the six; (e) shows the migration of micro-amounts of gadolinium, europium and prometheum detected by their activities and (f) shows the result obtained by subjecting the artificial mixtures composed according to Table 1 to electrophoresis. In all the above experiments the running time was 2 hr.

A few experiments were carried out with mixtures containing erbium as a representative of the higher lanthanons and yttrium. Neither yttrium nor erbium interfere with the isolation of gadolinium. The very specific electrophoretic behaviour of gadolinium observed in this study is difficult to explain. Neither complex formation between the lanthanons and the thioglycolic acid,[4] nor the half-filled 4f shell effect in gadolinium[5] can provide a plausible explanation. The basic strength of gadolinium may possibly play some part since, together with lanthanum, it belongs to the most basic elements of the series. If so, there is still the question why lanthanum behaves like the rest of the rare earths. The fact that gadolinium migrates to a lesser degree on paper than the other elements, one of the important factors governing the migration being the size of the migrating species, may be explained by the formation of gadolinium-mercaptoacetic compounds which incorporate hydroxo-molecules or which hold water molecules.

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[4] N. C. LI and R. MANNING, *J. Amer. Chem. Soc.* **77**, 5225 (1955); W. STRICKS, I. M. KOLTHOFF and D. HEYNDRICKS, *Ibid.* **76**, 1515 (1954); D. L. LEUSSIG and I. M. KOLTHOFF, *Ibid.* **75**, 3904 (1953).
[5] S. G. THOMPSON, B. B. CUNNINGHAM and G. T. SEABORG, *J. Amer. Chem. Soc.* **72**, 2798 (1950); E. I. WHEELWRIGHT, F. H. SPEDDING and G. SCHWARZENBACH, *Ibid.* **75**, 4196 (1953); G. SCHWARZENBACH and R. GUT, *Helv. Chim. Acta* **39**, 1589 (1956); W. NODDACK and G. OERTEL, *Z. Elektrochem.* **61**, 1216 (1957); D. F. PEPPARD, W. I. DRISCOLL, R. I. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).

On the preparation of anhydrous deuterium fluoride from fluorosulphonic acid and heavy water*

(*Received* 20 *February* 1959)

WE have recently described the preparation of anhydrous deuterium fluoride by the deuterolysis of various acyl fluorides.[1] It was found now that fluorosulphonic acid is a very convenient source of deuterium fluoride by the simple deuterolysis reaction

$$FSO_3H + D_2O = DF + DHSO_4$$

Although only half of the deuterium used is converted to DF, the reaction takes place at moderate temperatures and is practically quantitative at 100°C. As fluorosulphonic acid is commercially available this method is a convenient way to prepare pure, anhydrous deuterium fluoride.

EXPERIMENTAL

One hundred grammes (5 moles) deuterium oxide (99.77% purity from Atomic Energy of Canada Limited) was dropped into 1000 g (10 moles) of fluorosulphonic acid in an all metal (nickel, monel, platinum) distillation apparatus with exclusion of air moisture. The rate of addition was such that the temperature of the acid mixture could be maintained with cooling at 50–70°C while stirred with a Teflon covered magnetic stirrer. The DF formed was distilled off continuously and was collected

* Contribution No. 17.
[1] G. OLAH and S. KUHN, *Z. Anorg. Chem.* **287**, 282 (1956).

in a polyethylene receiver cooled in dry ice. After the addition was completed the acid mixture was warmed to 100°C for 1 hr while bubbling through dry nitrogen to complete the removal of the DF. The deuterium fluoride was redistilled. Yield 94·5 g (90%) b.p. 762 mm = 18·5°C. The reaction can also be carried out in a quartz glass apparatus. In this case, however, the product is contaminated with SiF_4 due to the etching of the silica and must be purified.

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LETTERS TO THE EDITORS

Phase separation through flotation in radiometric titration

(*Received* 9 *December* 1958)

RADIOMETRIC titration may be performed only when the labelled atom goes after the reaction into another phase. By following the radioactivity change one may determine the equivalence point. In the radiometric titrations described in the literature, precipitation reactions in which the labelled atom goes from a liquid (aqueous) into a solid (precipitate) phase[1] and complex forming reactions were used; the complexes formed in the latter reactions were insoluble in water, but soluble in organic solvents.

TABLE 1

Flotant	$[MP_n](SCN)_2$					Mercaptobenzthiazole					$[Hg(SCN)_4]Me$		
	Cu	Co	Ni	Cd	Zn	Cu	Ag	Bi	Cd	Au	Cu	Co	Zn
Ether	+	+	+	+	+	+	−	*S*	*S*	+	−	−	+
CCl_4	+	+	+	+	+	+	−	+	*S*	−	−	−	+
Butanol	+	+	+	+	−	−	−	−	−	+	+	+	+
Amyl alcohol	+	+	+	−+	−						−	−	+
Butanol + CCl_4							+			+			
Acetylacetone											−	−	+
Ether + CCl_4											+	+	+
Cresol + CCl_4											+	−	−

	$MeCrO_4$		$MeIO_3$
CCl_4 + butanol + cresol	Ag	Pb	Ag
	+	+	
Amyl alcohol			−
Ethyl acetate			−
Acetylacetone			−
CCl_4			−
CCl_4 + cresol			+

Notation: + = flotation; − = not flotation; *S* = solubilization of the precipitate.

In the precipitation reactions, phase separation was achieved through filtration,[1] centrifugation[2] or centrifugation and filtration.[3] In the complex forming titration, the separation may be carried out through extraction with organic solvents.[4] However these methods exhibit some disadvantages. Separation via filtration may become difficult through blockage of the filter; the separation of very fine precipitates through centrifugation is often not complete. The main disadvantage in the separation via extraction with organic solvents is its limitation; this procedure has been applied actually only to dithizone complexes.

[1] A. LANGER, *J. Phys. Chem.* **45**, 639 (1941).
[2] I. M. KORENMAN *et al.*, *Zavodsc. Lab.* **22**, 1143 (1956).
[3] A. LANGER, *Analyt. Chem.* **22**, 1288 (1950).
[4] I. M. KORENMAN *et al.*, *Z. Anal. Himii* **12**, 48 (1957).

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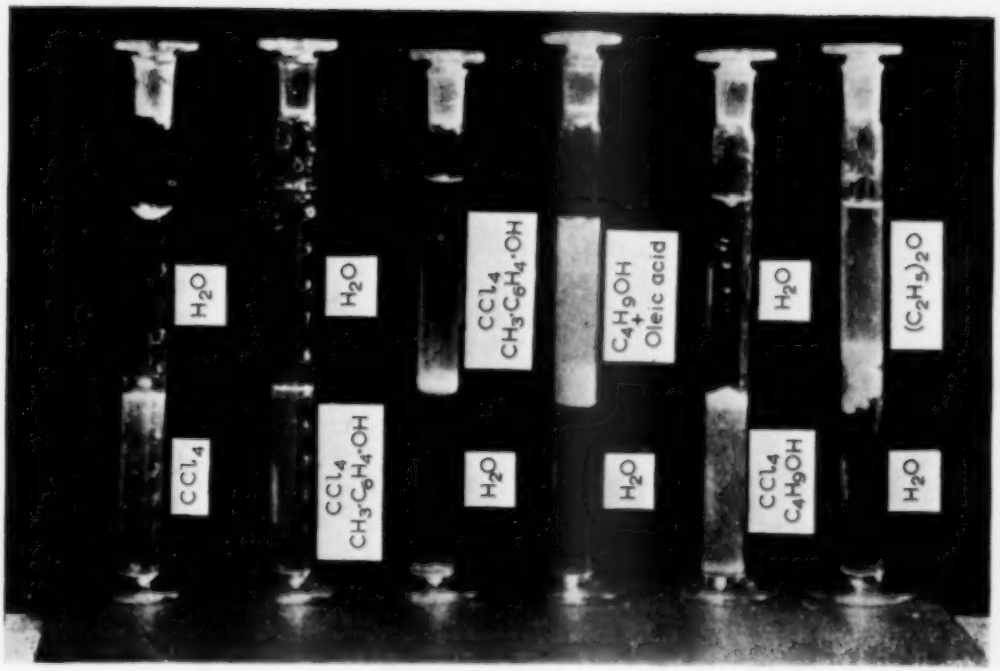

FIG. 1. Flotation of $[CoPy_4](SCN)_2$ precipitate in various flotation reagents.

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The purpose of the authors was to find a more rapid and efficient procedure for the separation of the silver iodate precipitate in the radiometric titrations with complexon III of some cations.[5,6] In the present work, a new procedure for the separation of $AgIO_3$, which may be applied to all precipitates formed during radiometric titration, is described. This procedure is based upon the flotation phenomenon, which may be defined as the separation of the solid phase from an aqueous solution through adhesion, owing to the interfacal tensions of the solid particles found at the surface of air bubbles in the suspension. The system consists of three phases: a gaseous (air bubbles), a liquid (water) and a solid (solid particle) phase. The separation of the solid precipitate from the aqueous solution can take place by a similar mechanism in a different system, where the gaseous

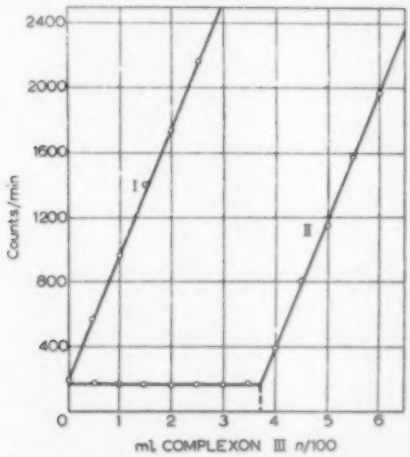

FIG. 2.—Radiometric titration of the $Ag \times IO_3$ indicator (I) and of magnesium in the presence of $Ag \times IO_3$ (II). Phase separation: flotation with CCl_4.

phase is replaced by a liquid phase which is not mixable with water such as an organic compound. Through stirring, the two phases form an unstable emulsion of the organic compound in water. Owing to the interfacal tensions, the precipitate grains adhere to the surface of the drops of organic compound and finally are separated at the interface of the two liquids. If the organic phase wets the precipitate more efficiently than water, the precipitate does not remain at the interface, but spreads into the organic phase. The aqueous solution layer remains clear and may be above or below the organic phase, depending on the density. The activity measurement is performed more conveniently when the labelled atoms are in the upper phase. Because one has to determine the aqueous phase activity, it is suitable to use flotation substances with a specific gravity greater than that of the working phase. Fig. 1 shows the flotation of the $[CoPy_4](SCN)_2$ precipitate, in various flotation liquids. (With this procedure many precipitates may be separated from the aqueous solution, provided a suitable flotation substance is found and, eventually, some auxiliary reagents used as emulsifiers and collectors). As a flotation phase, either an organic compound immiscible with water, or a mixture of organic compounds which may be miscible with each other but not with water, may be used.

The separation of some precipitates of various cations with organic precipitants was tried using various flotation phases. The qualitative results obtained are given in Table 1.

The separation through flotation is, in the authors' opinion easier to perform, more rapid and more clear than separation via filtration or centrifugation; it has wider applicability than separation by solvent extraction.

In the following, two examples of radiometric titration with phase separation through flotation are given. The first refers to magnesium titration with complexon III using silver iodate labelled with ^{110}Ag as a non-isotopic tracer in a heterogenous phase.[6] From Table I it may be seen that the

[5] T. BRAUN, I. MAXIM and I. GĂLĂTEANU, *Nature, Lond.* **182**, 936 (1958).
[6] T. BRAUN, I. MAXIM and I. GĂLĂTEANU, *Z. Anal. Himii.* To be published.

silver iodate flotation is carried out satisfactorily with a mixture of carbon tetrachloride and cresol in a ratio of 5 : 1. Fig. 2 shows the titration curves of silver iodate with complexon III (curve I) and with magnesium ions (curve II). Similar success was gained in the titration of cobalt labelled with ^{60}Co with potassium thiocyanate resulting in the insoluble complex $[CoPy_4](SCN)_2$ and in the titration of nickel also labelled with ^{60}Co resulting in $[NiPy_4](SCN)_2$ which coprecipitates with $[CoPy_4](SCN)_2$. The flotation reagent was carbon tetrachloride.

Finally we may mention that phase separation through flotation may be used successfully not only in radiometric titrations but also in other radiochemical problems like solubility product determinations, coprecipitation studies or isotopic exchange in heterogenous media.

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The relation between the C≡N stretching frequency and Hammett's σ

(*Received* 23 *December* 1958)

RECENTLY a paper was published[1] which discussed the position of the C≡N stretching frequency in terms of the inductive and mesomeric effects of substituent groups. Since Hammett's σ is a measure of this power, one expects it to be related to the C≡N stretching frequencies. Whereas the type of

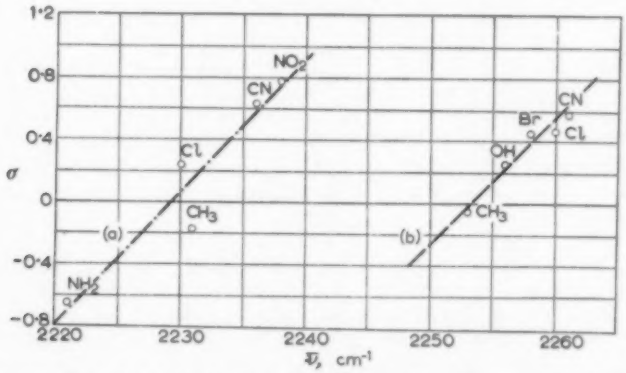
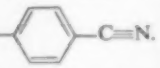
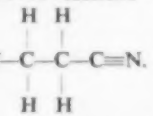


FIG. 1. The relationship between the C≡N stretching frequency and Hammett's σ

relation that exists between the C=O stretching frequencies and Hammett's σ has been thoroughly investigated,[2,3] the type of relation between the stretching frequencies of the isoelectronic CN group and the mentioned structural parameter has not yet been investigated.* The purpose of this communication is to examine such relation.

* The relation between the infra-red intensity of this group and Hammett's σ has been examined by some workers, eg. T. Brown, *J. Amer. Chem. Soc.* **80,** 794 (1958).

[1] M. F. EL SAYED and R. SHELINE, *J. Inorg. Nucl. Chem.* **6,** 187 (1958).
[2] R. H. GILLETTE, *J. Amer. Chem. Soc.* **58,** 1143 (1936).
[3] M. ST. C. FLETT, *Trans. Faraday Soc.* **44,** 767 (1948).

Fig. 1(a) shows the relationship found between the σ_{para}[4] of X and the infra-red C≡N stretching frequencies[5] of compounds of the type  . Fig. 1(b) shows the relationship between the $\sigma_{inductive}$[6] of X and the infra-red C≡N stretching frequencies[5] of compounds of the type  . It is important to notice that the lines (a) and (b) in Fig. 1 are both straight and parallel to each other and are separated by ~25 cm^{-1}. This is the same value found for the lowering of the CN stretching frequency[5,3] due to mesomeric or conjugation resonance.

It is also important to mention that whereas the straight lines obtained for this relation for both the nitriles and the carbonyls have positive slopes, those observed between the OH stretching frequencies and Hammett's σ for the phenols[7] have negative slopes. The reason for this is the fact that groups that increase the contribution of the ionic resonating structures in the former compounds decrease them in the latter ones (phenols) and consequently they will have opposite effects on the stretching frequencies in the two cases.

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[4] J. H. JAFFE, *Chem. Rev.* **53,** 193 (1953).
[5] R. E. KISTON and N. E. GRIFFITH, *Analyt. Chem.* **24,** 334 (1952); Frequencies reported are accurate to ±0·5 cm^{-1} (Private Communication).
[6] M. S. NEWMAN, *Steric Effects in Organic Chemistry*, p. 595. Wiley, New York (1956).
[7] L. L. INGRAHAM, J. CORSE, G. F. BAILEY and F. STITT, *J. Amer. Chem. Soc.* **74,** 2297 (1952).

J. Inorg. Nucl. Chem., 1959, Vol. 10, p. 170. Pergamon Press Ltd. Printed in Northern Ireland

Books Received

Report of the FBI Conference on Nuclear Energy held at Eastbourne 10–12 *April* 1958. Federation of British Industries, London, 1958.

D. J. E. INGRAM: *Free Radicals as Studied by Electron Spin Resonance*. Butterworths Scientific Publications, London, 1958.

J. C. GHOSH, S. K. BHATTACHARAYYA and M. V. C. SASTRI: *Some Catalytic Gas Reactions of Industrial Importance*. Oriental Institute, Baroda, 1958.

Tables of Interatomic Distances and Configuration in Molecules and Ions. Compiled by H. J. M. BOWEN *et al*. Special Publication No. 11 of The Chemical Society, London, 1958.

Vacancies and Other Point Defects in Metals and Alloys (A Symposium). The Institute of Metals, London, 1958.

CARLOS G. BELL, JR. and F. NEWTON HAYES: *Liquid Scintillation Counting*. Pergamon Press, London, New York, 1958.

E. SEGRÉ (Editor): *Annual Review of Nuclear Science* Vol. 8. Annual Reviews, Calif., 1958.

F. S. MARTIN and G. L. MILES: *Chemical Processing of Nuclear Fuels*. Butterworths Scientific Publications, London; Academic Press, New York, 1958.

J. V. JELLEY: *Čerenkov Radiation and its Applications*. Pergamon Press, London, New York, 1958.

RUDOLF SCHRADER: *Die Wirkungen von Explosionen*. Verlag Soldat und Technik, Frankfurt am Maim, 1958.

GLENN T. SEABORG: *The Transuranium Elements*. Addison-Wesley, Reading, Mass., 1958.

J. K. DAWSON and G. LONG: *Chemistry of Nuclear Power*. (Newnes Technical Survey). George Newnes, London, 1959.

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Papers to be published in future issues

R. A. SHARP and A. C. PAPPAS: ^{113}Cd Isomer yield ratios from deuteron fission of ^{235}U and from the ^{116}Sn(d, αp), ^{116}Sn(n, α), ^{115}In(d, $2p$), ^{115}In(n, p), and ^{114}Cd(d, p) reactions from 10 to 25 MeV.

W. HÜBEL und E. H. BRAYE: Organometallic complexes—IV. Über die Reaktion von substituierten Acetylenverbindungen mit Eisentetracarbonyl.

M. A. FINEMAN and R. DAIGNAULT: Electronegativaties calculated using a modification of Pauling's equation.

C. J. HARDY and D. SCARGILL: Studies on mono- and di-*n*-butylphosphoric acids—I. The separation of mono- and di-*n*-butylphosphoric acids by solvent extraction and by paper chromatography.

D. HALL and G. N. WALTON: Chemical effects in fission recoil—IV. The efficiency of recoiling atoms in the decomposition of potassium nitrate.

R. SKOCHDOPOLE and S. CHABEREK: Iron chelates of N-hydroxyethylethylenediaminetriacetic acid.

J. D. KNIGHT, D. C. HOFFMAN, B. J. DROPESKY and D. L. FRASCO: Radiations of ^{93}Y and ^{94}Y and half-lives of ^{93}Sr and ^{94}Sr.

E. WEISS and W. HÜBEL: Organometallic complexes—V. π-Komplexe ans cyclischen Dienverbindungen und Metallcarbonylen.

H. IRVING and D. N. EDGINGTON: The extraction of some metal chlorides into tri-*n*-butyl phosphate.

A. T. CASEY and A. G. MADDOCK: The chemistry of protactinium—V. A comparison of the extraction of protactinium, niobium and tantalum.

J. VANDEGAER, S. CHABEREK and A. E. FROST: Iron chelates of diethylenetriaminepentaacetic acid.

R. HARDER and S. CHABEREK: The interaction of rare earth ions with diethylenetriaminepentaacetic acid.

S. CHABEREK, A. E. FROST, M. A. DORAN and N. J. BICKNELL: Interaction of some divalent metal ions with diethylenetriaminepentaacetic acid.

D. F. PEPPARD and J. R. FERRARO: The preparation and infra-red absorption spectra of several complexes of bis-(2-ethylhexyl)-phosphoric acid.

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^{115}Cd ISOMER YIELD RATIOS FROM DEUTERON FISSION OF ^{238}U AND FROM THE ^{118}Sn($d,\alpha p$), ^{118}Sn(n,α), ^{115}In($d,2p$), ^{115}In(n,p), AND ^{114}Cd(d,p) REACTIONS FROM 10 TO 25 MeV

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Abstract—The isomer yield ratio of ^{115m}Cd($\frac{11}{2}-$) to ^{115g}Cd($\frac{1}{2}+$) has been investigated for the reactions ^{238}U(d,f), ^{118}Sn($d,\alpha p$) and (n,α), ^{115}In($d,2p$) and (n,p) and ^{114}Cd(d,p) from 10 to 25 MeV. The results are discussed in terms of several spin important mechanisms. The minimum in the isomer yield ratio vs. energy for ^{238}U(d,f) is consistent with a proposal involving increased fission barrier penetration for high-spin compound nuclei in symmetric fission at low excitation energies.

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IN order to further investigate the spin dependence of nuclear reaction yields, the isomer yield ratio of independently formed (primary) 53 hr ^{115g}Cd and 43 day ^{115m}Cd was studied as a function of energy for several nuclear reactions. The deuteron and neutron induced reactions leading to ^{115}Cd which were energetically possible with the projectiles available and natural uranium, tin, indium, and cadmium as targets are summarized in Table 1. The reaction thresholds given are based on the reaction Q values computed from the masses of the participating nuclei and on the height B of the barrier at its maximum value. Two threshold values are given: $-Q + B_p + B\alpha$ being the classical threshold assuming zero spin for the projectile and no barrier penetration, and: $-Q + 0{\cdot}5B_p + 0{\cdot}7B\alpha$ being a lower practical threshold selected on the basis of about 1 per cent barrier penetration.[1]

From Table 1 it can be seen that for 25 MeV deuterons and neutrons and most combinations of target and projectile, only one mechanism is important to the observed yield. Exceptions occur for deuterons on cadmium and neutrons on tin. The ^{116}Cd($d,p2n$)^{115}Cd reaction has a rather low threshold and will therefore interfere with the predominant ^{114}Cd(d,p)^{115}Cd reaction above ~18 MeV. Similarly the ^{119}Sn($n,\alpha n$)^{115}Cd reaction will interfere with the ^{118}Sn(n,α)^{115}Cd reaction above ~22 MeV. But the low isotopic abundance ratio of ^{116}Cd to ^{114}Cd and ^{119}Sn to ^{118}Sn (0·26 and 0·36 respectively) reduce the interference considerably.

1. EXPERIMENTAL

Irradiation techniques

All bombardments were done with the 200 cm cyclotron at the Nobel Institute of Physics, Stockholm, Sweden. Target materials were Merck reagent grade tin metal and cadmium chloride, Johnson

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[1] J. BLATT and V. F. WEISSKOPF, *Theoretical Nuclear Physics*. John Wiley, New York (1952).

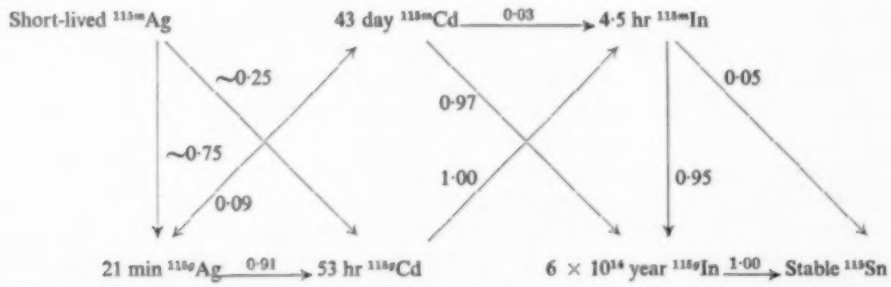
Mathey "specpure" indium oxide, and nitrate-free uranium trioxide prepared from Merck reagent grade uranyl nitrate by a method described elsewhere.[2]

For the deuteron bombardments, ~50 mg samples of targets were individually compressed into 1 cm² depressions in copper plugs and held in place by 13–15 μ platinum foils. The plugs were screwed into an oscillating water-cooled probe exposed directly to the internal circulating deuteron beam. About 2–4 μ A of beam current per target could be tolerated without burning through the platinum cover foil. Deuteron bombarding energies were calculated from the known constants of the accelerator and corrected for absorption in the platinum foil and target material by interpolation of the range energy curves of ARON *et al.*[3] Target width and thickness introduced an uncertainty in the calculated energy from ~0·5 MeV (at 25 MeV) to ~1·1 MeV (at 10 MeV). The energy distribution of the deuteron beam was not known precisely but the half width was probably 2–3 MeV at the energies used.

The neutrons were obtained by the well known $^{9}Be(d, n)^{10}B$ reaction. The targets were sealed in Tygon capsules which were placed in an aluminium tube at a 90° angle close to a thick water-cooled beryllium target. The neutron flux at the targets was approximately 10^{10} cm^{-2} sec^{-1}. The "neutron energies" quoted are the calculated incident deuteron energies. The actual neutron spectrum in the target arrangement used was complex and extended from ~3 MeV above the deuteron energy to near zero values, but the effective neutron energy was roughly proportional to the deuteron energy.

Chemical separations

Twenty-one minute ^{115}Ag is formed in high yield in deuteron fission of uranium at these energies and the mass 115 fission product chain constructed from published data forms a rather complicated picture:



^{115g}Ag feeds the ^{115m}Cd/^{115g}Cd isomers by β-decay to the two states in the ratio of 1 : 10 respectively[4] thus interfering seriously with the observation of independently formed ^{115g}Cd and ^{115m}Cd. Other reactions leading to ^{115}Ag (see Table 1) interfered with the studies on cadmium targets. A search was made for a fast and clean separation of cadmium from silver which would hopefully also give good decontamination from fission products in the case of uranium targets, i.e. from the elements from zinc through dysprosium. The decontamination problems in the low energy deuteron fission of ^{238}U are severe since ^{115}Cd is located at the minimum of the fission-product mass distribution curve. For targets of tin, indium, and cadmium, however, only decontamination from the elements palladium through antimony was needed.[5]

WELCHER's compilation[6] suggested that diphenylthiocarbazone (dithizone) might be a useful reagent for this purpose. Dithizone is essentially a heavy metal reagent and of the elements formed in the bombardments used only Sn^{2+}, In^{3+}, Cd^{2+}, Ag^{+}, and Pd^{2+} were reported to form chloroform-extractable complexes with dithizone. The conditions of extraction for these elements are given in Table 2.

[2] A. C. PAPPAS, *A Radiochemical Study of Fission Yields in the Region of Shell Perturbations and the Effect of Closed Shells in Fission*, AECU-2806. Technical Report No. 63, Laboratory for Nuclear Science and Engineering, M.I.T. (1953).
[3] W. A. ARON, B. G. HOFFMAN, F. C. WILLIAMS, *Range Energy Curves* (2nd Revision), UCRL Report AECU-663 (1951).
[4] A. C. WAHL and N. A. BONNER, *Phys. Rev.* **85**, 570 (1952).
[5] H. G. HICKS and R. S. GILBERT, *Phys. Rev.* **100**, 1286 (1956).
[6] F. J. WELCHER, *Organic Analytical Reagents* Vol. 3, p. 463. Van Nostrand, New York (1947).

TABLE 1.—REACTION THRESHOLDS

Reaction	Q (MeV)	$-Q + B_p + B\alpha$ (MeV)	$-Q + 0{\cdot}5B_p + 0{\cdot}7B\alpha$ (MeV)
^{238}U(d, f) fission fragments ~	+180	15[a]	7[a]
^{118}Sn(d, αp)^{115}Cd	−2·1	30	20
^{119}Sn(d, αpn)^{115}Cd	−9·5	37	27
^{115}In(d, $2p$)^{115}Cd	−2·9	23	13
^{114}Cd(d, p)^{115}Cd	+6·2	10[a]	5[a]
^{116}Cd(d, $p2n$)^{115}Cd	−10·4	20	15
^{118}Sn(n, α)^{115}Cd	+0·1	18[c]	13[c]
^{119}Sn(n, αn)^{115}Cd	−7·3	25	20
^{116}Sn(n, $2p$)^{116}Cd	−9·6	30	20
^{120}Sn(n, $\alpha 2n$)^{115}Cd	−16·5	35	30
^{117}Sn(n, $2pn$)^{115}Cd	−19·7	40	30
^{115}In(n, p)^{115}Cd	−0·7	10	5
^{116}Cd(n, $2n$)^{115}Cd	−8·2	8	8
^{116}Cd(d, $2pn$)^{115}Ag	−10·4	30[b]	20[b]
^{116}Cd(n, pn)^{115}Ag	−8·1	18[b]	13[b]

[a] Threshold governed by barrier to incident deuteron.
[b] Decays by negatron emission to ^{115}Cd thus interfering with ^{115}Cd independent yields.
[c] Threshold governed by barrier to evaporated alpha.

TABLE 2.—DITHIZONATE EXTRACTIBILITIES

Element	pH for some extraction	pH for complete extraction	Colour in $CHCl_3$	Formula of extracted species
Sn^{2+}	0–10	3·5–8·5	purple-red	$SnDz_2$
In^{3+}	—	5–6	red	~$InDz_3$
Cd^{2+}	9·5–14	>12·2	red	$CdDz_2$
Ag^{+}	>0	>1·5	yellow	$AgDz$
Pd^{2+}	weakly acid	incomplete	violet or brown	$PdDz_2$

Table 2 is the result of mostly qualitative observations by many different workers and while only useful as a guide it does indicate that a strongly basic chloroform extraction of cadmium dithizonate might give high radiochemical purity.

Using pile-produced antimony, tin, indium, cadmium, silver, and palladium tracers and a Harshaw Type 22 NaI(Tl) well scintillation counter to assay the liquid phases, the extractive behaviour of these metals was studied under a wide variety of conditions. It was found that cadmium extracted with high efficiency from strongly basic solutions and that only silver interfered appreciably when tartrate was present to prevent hydroxide precipitation. This interference was due partly to colloidal silver oxide particles entrained in the organic layer. Addition of potassium cyanide to complex the silver prevented its extraction without interfering with the recovery of cadmium. A strongly reducing hydroxylamine environment was maintained in all of these experiments to prevent oxidation of the rather unstable dithizone. In the procedure finally adopted and given below two extraction cycles were used. More than 95 per cent of the cadmium was recovered from the final organic phase with decontamination factors of $>10^4$ with respect to antimony, tin, indium, silver, and palladium.

The targets were dissolved immediately after bombardment (UO_2 and Sn in conc HCl, In_2O_3 and $CdCl_2$ in 6 N HCl). To the hot target solution were added 0·500 mg Cd^{2+} carrier (except in the

case of the $CdCl_2$ target) and 0·1 mg each of the carriers Sn^{2+}, In^{3+}, Ag^+ and Pd^{2+}. To this was added 10 ml of solution *A* (*A* = 100 mg/ml NH_3OH, 100 mg/ml potassium sodium tartrate, and 2 mmoles/ml KOH) followed by 5 drops 1 M KCN and an amount of KOH equivalent to the HCl used. The solution was then made up to 30 ml with water and extracted with 30 ml of solution *B* (*B* = 0·1 mg dithizone/ml $CHCl_3$) by vigorous shaking for 30 sec in a separatory funnel. The phases were then separated and the aqueous phase extracted with successive 10 ml portions of solution *B* until the extracts were colourless (usually four extractions were necessary). The time of the last extraction was taken as the time of the separation of cadmium from silver. The organic phases were combined and washed once with 30 ml of solution *C* (*C* = 10 ml *A* + 20 ml H_2O which has been equilibrated with 10 ml *B*). Quantitative recovery of the aqueous phase was essential as any loss was reflected in the subsequent determination of the amount of ^{115}Cd formed from the decay of ^{115}Ag. About 8–10 min was required to finish this part of the procedure.

The organic and aqueous phases were then put aside for 24 hr to allow 2·9 hr ^{117}Cd and 21 min ^{115}Ag to decay and then treated in the following way: (i) The organic phase (containing ^{115}Cd) was back extracted with 20 ml 0·25 M HCl and the organic phase discarded. After adding 12 ml *A*, 5 drops 1 M KCN and 0·1 mg each of the carriers Sn^{2+}, In^{3+}, Ag^+ and Pd^{2+}, the aqueous phase was extracted with 30 ml of solution *B* followed by three more extractions with 10 ml portions of solution *B*. The organic phases were combined and back extracted with 20 ml 0·25 M HCl. The back extracts were neutralized to phenol-red end point with dilute NaOH. Red crystalline Cd(dithizonate)$_2$ was then precipitated by adding an equal volume of 2 M NaOH containing 3 mg of freshly dissolved dithizone. After heating to boiling and cooling to coagulate the precipitate, the slurry was vacuum filtered onto fine filter paper, washed with water, ethanol, and ether and dried under a heat lamp preparatory to mounting.

(ii) To the aqueous phase from the original cadmium–silver separation was added 0·500 mg Cd^{2+} carrier and 7 ml conc HCl. The free dithizone was then extracted with chloroform. After neutralizing with KOH and adding 10 ml of solution *A* and 5 drops of 1 M KCN, the cadmium in the aqueous phase was extracted. The cadmium was back extracted and precipitated as described in the last paragraph. In those bombardments where no ^{115}Ag was formed, the aqueous phase was discarded after the initial cadmium–silver separation.

The ^{115}Cd samples were allowed to stand for at least 48 hr after precipitation to allow the 4·5 hr ^{115m}In daughter activity to attain radioactive equilibrium. When counting had been completed, the cadmium carrier was recovered from the samples by digesting the filter paper with boiling 6 M HCl. After filtering, the solution was extracted once with an equal volume of chloroform to remove residual dithizone. The cadmium chemical yield was determined colorimetrically with dithizone following the procedure of SANDELL.[7] The high efficiency of the extraction purification and high sensitivity of the colorimetric yield determination made it practical to use very small amounts of carrier. The resulting thin samples (<0·5 mg/cm^2) allowed the use of simplified counting corrections.

Counting techniques

The cadmium dithizonate precipitates were deposited evenly over a 5 cm^2 area by vacuum filtration onto 17 mg/cm^2 filter paper backed with 9 mg/cm^2 Scotch tape and covered with 3 mg/cm^2 polystyrene film. Counting was done with a thin mica end-window Geiger tube (Tracerlab TGC 2, 1·9 mg/cm^2) in a conventional aluminium shelf and lead castle counting arrangement.[8] The decay of the cadmium samples was followed for five months and the decay curves resolved into the 54 hr and 43 day components. No evidence of contamination by activities of other half-lives was found and Feather analysis of aluminium absorption curves verified the published values of the β-particle energies.[8]

CALCULATIONS AND RESULTS

The raw counting data were corrected for background and coincidence loss and the gross decay curves resolved into components which were extrapolated back to the middle of bombardment (*A* values). As both irradiation and decay times were short (10 min) as compared to the half-lives in question, the yield ratio of ^{115m}Cd to ^{115g}Cd

[7] E. B. SANDELL, *Colorimetric Determination of Traces of Metals* (2nd Ed.) p. 230. Interscience Publishers, New York (1950).
[8] J. M. HOLLANDER, I. PERLMAN and G. T. SEABORG, *Rev. Mod. Phys.* **25**, 469 (1953).

(σ_m/σ_g) can be calculated from standard equations[2] for the atoms present after a bombardment of length t_1 and a decay time t_2 from end of bombardment to time of the fast separation of cadmium from silver. The simplified equation is:

$$\frac{\sigma_m}{\sigma_g} = \frac{\left\{A_1 Y_a - A_3 Y_0\left[\dfrac{\lambda t_1 - \{\exp(-\lambda t_2) - \exp -\lambda(t_1 + t_2)\}}{\exp(-\lambda t_2) - \exp -\lambda(t_1 + t_2)}\right]\right\} T_{\frac{1}{2}}{}^m f_W{}^g f_B{}^g f_C{}^g}{\left\{A_2 Y_a - A_4 Y_0\left[\dfrac{\lambda t_1 - \{\exp(-\lambda t_2) - \exp -\lambda(t_1 + t_2)\}}{\exp(-\lambda t_2) - \exp -\lambda(t_1 + t_2)}\right]\right\} T_{\frac{1}{2}}{}^g f_W{}^m f_B{}^m f_C{}^m}$$

where

A_1 = observed A for ^{115m}Cd in the organic sample

A_2 = observed A for ^{115g}Cd in the organic sample

A_3 = observed A for ^{115m}Cd in the aqueous sample

A_4 = observed A for ^{115g}Cd in the aqueous sample

Y_0 = chemical yield for the organic phase sample

Y_a = chemical yield for the aqueous phase sample.

where "organic" and "aqueous" phases refer to the independent ^{115}Cd rich and the daughter ^{115}Cd rich fractions respectively from the fast cadmium–silver separation. The exponential terms in square brackets correct for saturation effects in the buildup of ^{115}Ag during the bombardment and for the subsequent decay of ^{115}Ag from the end of bombardment to the time of the fast cadmium–silver separation. λ is the decay constant of ^{115}Ag.

The $T^m_{1/2}$ and $T^g_{1/2}$ refer to the 43 day and 53 hr half-lives of ^{115m}Cd and ^{115g}Cd respectively. The factors $f_W{}^m$ and $f_W{}^g$ correct for air, counter window and sample cover absorption as f_W = (observed activity with absorption)/(true activity with no absorption) and were measured by extrapolation of first shelf aluminium absorption curves to zero total absorber, giving $f_W{}^g/f_W{}^m = 0{\cdot}91 \pm 0{\cdot}02$.

The f_B's correct for backscattering of electrons from the filter paper–Scotch tape backing. From the curves of YAFFE and JUSTUS,[9] it is found that $f_B{}^g/f_B{}^m = 1{\cdot}00 \pm 0{\cdot}02$. Effects due to air and shield scattering could be assumed invariant for radiation studies.[2,10] The sample precipitates showed a fine and evenly deposited microstructure. Sample absorption and scattering effects for the thin sources ($\sim$0·5 mg/cm^2) used were found negligible and in any case tended to cancel. The f_C factors are counting efficiencies calculated as f_C = (no. of β-particles per decay + 0·01 $\times$ no. of γ per decay) as in the small geometry used here the number of coincidences are small and can be neglected. The decay scheme of reference (8) is assumed valid.

For those bombardments where no interfering ^{115}Ag was produced, A_3 and $A_4 = 0$, the exponential terms drop out and no chemical yields need to be known. The results are summarized in Table 3.

The errors quoted for σ_m/σ_g include a 4 per cent combined error on the factors $T_{1/2}$, f_W, f_B and f_C and a 1 per cent error on Y_a and Y_0. The remaining error arose principally from the difficulties in measuring the low activities obtained with the necessarily short bombardments used (10 min) and the low maximum beam currents that could be tolerated.

[9] L. YAFFE and K. M. JUSTUS, *J. Chem. Soc.* suppl. No. 72, 5341 (1949).
[10] L. R. ZUMWALT, ORNL Report AECU-567 (1950).

Attempts were made to measure the $^{238}U(n,f)^{115}Cd$ reaction but the neutron fluxes available were inadequate for this purpose. Similarly not enough 43 day ^{115m}Cd for accurate measurement could be produced by the $^{116}Cd(n,2n)^{115}Cd$ reaction. Only small aliquots of the cadmium targets could be tolerated under the separation and counting correction schemes used, and this difficulty combined with the low natural abundance of the ^{116}Cd target isotope (7·6 per cent) precluded study of this reaction.

TABLE 3.—σ_m/σ_g VALUES

Reaction	Projectile, energy (MeV)	Target, spin and parity	Compound nucleus, possible spin and parity	σ_m/σ_g
$^{238}U(d,f)^{115}Cd$	10	0+	1+	0·30 ± 0·08
	15			0·15 ± 0·02
	20			0·071 ± 0·008
	25			0·025 ± 0·003
$^{115}Sn(d,\alpha p)^{115}Cd$	25	0+	1+	1·31 ± 0·22
$^{115}Sn(n,\alpha)^{115}Cd$	15	0+	1/2+	1·24 ± 0·17
	20			0·60 ± 0·07
	25			0·75 ± 0·11
$^{115}In(d,2p)^{115}Cd$	15	9/2+	7/2, 11/2+	3·19 ± 0·23
	20			2·40 ± 0·35
	25			1·08 ± 0·15
$^{115}In(n,p)^{115}Cd$	10	9/2+	4, 5+	1·0 ± 0·3
	15			0·90 ± 0·21
	20			0·60 ± 0·10
	25			0·53 ± 0·06
$^{114}Cd(d,p)^{115}Cd$	10	0+	1+	0·69 ± 0·07
	15			0·29 ± 0·03
	20			0·23 ± 0·02
	25			0·109 ± 0·011

DISCUSSION

It has been shown that many factors influence isomer yield ratios in nuclear reactions.[11] At low energies and to some extent at moderate energies the spins of the target and final nuclei are important and tend to favour production of the isomer closest in spin to that of the compound nucleus. But as higher energy particles are captured to form the compound nucleus and as more energetic and greater numbers of particles are emitted during its breakup, larger transfers of angular momentum will occur which will tend to increase the relative yield of the initially unfavoured state. γ cascades in highly excited compound nuclei provide a further mechanism for bridging large differences between target and isomer spins. In each of the above three processes a statistical weighing factor enters which favours the production of high-spin states and thus the greatest *changes* in isomer yield ratios with energy are expected for targets of low relative spin. As suggested by LEVY,[12] the above considerations alone imply a steadily increasing predominance of the high spin isomer with increasing energy. But the onset of knock-on processes with increasing energy forms residual

[11] J. W. MEADOWS, R. M. DIAMOND and R. A. SHARP, *Phys. Rev.* **102**, 190 (1956).
[12] H. B. LEVY, UCRL Report UCRL-2305 (1953).

nuclei of low excitation and low spin and this fact plus the probable rarity of high spin states in excited nuclei (especially in final nuclei of <10 MeV excitation)[11] tends to counteract the first three effects by increasing the yield of the low spin products with increasing energy.

Detailed separation of these effects is difficult enough for reactions with simple projectiles but in the case of deuteron bombardments further ambiguities arise when only one constituent of the deuteron is absorbed in the initial interaction (Oppenheimer–Phillips process). Thus three compound nuclei can be formed by the deuteron bombardment of a target (Z,A): (1) $(Z+1,\ A+2)$; (2) $(Z+1,\ A+1)$ and (3) $(Z,\ A+1)$ with (3) being especially important at low energies where barrier repulsion is important. This multiplicity of paths tends to smear out any restrictions due to spin and parity considerations.

Table 3 gives the spin and parity of the target and compound nuclei near threshold (capture of $l=0$ neutrons and deuterons only). Since the cadmium isomers have spins and parities of $\frac{11}{2}-$ and $\frac{1}{2}+$ for the ^{115m}Cd and ^{115g}Cd respectively, it would be reasonable to expect a high σ_m/σ_g value for a high spin target near threshold with σ_m/σ_g decreasing with increasing energy. Such is the case for the In$^{115}(d,2p)^{115}$Cd reaction. A similar initial high σ_m/σ_g value is not found for the high spin target in the ^{115}In$(n,p)^{115}$Cd reaction. This difference may be largely due to the higher residual excitation in the ^{115}Cd final nucleus allowing greater opportunity for spin adjustment by γ-cascade. Also, the increased restrictions due to centrifugal barrier effects for charged particles with $l>0$ are a much greater handicap to high-spin changes in the $(d,2p)$ reaction where two more charged particles are involved than in the (n,p) case.

The ^{115}In$(n,p)^{115}$Cd and ^{114}Cd$(d,p)^{115}$Cd reactions involve the same compound nucleus but with higher spin in the first case which has the effect of giving higher ^{115m}Cd yields. But the last reaction shows the greatest changes in σ_m/σ_g near threshold in accordance with what one would expect on the basis of the previous discussion.

The ^{118}Sn$(n,\alpha)^{115}$Cd is the least energy dependent of all the reactions listed. This may reflect the reduced centrifugal barrier effects for α-particles as compared to protons.

The σ_m/σ_g values for the ^{238}U$(d,f)^{115}$Cd reaction have been plotted vs. energy in Fig. 1 including also the recent data of HICKS and GILBERT[5] for the same reaction in the 50 MeV to 190 MeV range. The striking minimum observed is in contradiction to the explanation advanced by HICKS and GILBERT which predicted a continued decrease in ^{115m}Cd production with decreasing energy by means of an argument similar to that advanced by LEVY.[12]

The excitation functions of HICKS and GILBERT indicated that while ^{115m}Cd measured with due attention to eliminating interferences from 21 min ^{115}Ag decay was indeed independently formed, the ^{115g}Cd recovered was apparently largely the result of decay from higher members of the mass 115 chain which decay via a short-lived ^{115m}Ag metastable state. Indirect evidence for such a short-lived ^{115m}Ag which decays *exclusively* to the ground state of ^{115}Cd with a half-life of less than 3 min was found by WAHL and BONNER.[4]

DZELEPOV and PEKER[13] point out that on the basis of their decay scheme, spin and log ft. considerations preclude a direct β-transition from the spin $\frac{1}{2}$ ground state

[13] V. S. DZELEPOV and L. K. PEKER, *Publication of the Academy of Sciences of the U.S.S.R.* Moscow 1957; issued as AECL-457 (translation), Chalk River, Ont. (1957).

of 21 min ^{115}Ag to the spin $\frac{11}{2}$ excited state of 43 day ^{115m}Cd. The ^{115m}Cd must be formed from a higher energy low spin level or levels in cadmium formed directly by beta decay from the 20 min silver. Recently CORYELL *et al.*[14] reported observing ~20 sec ^{115m}Ag in the mass 115 fission product chain. They assigned a spin of $\frac{1}{2}-$ to ^{115m}Ag and $\frac{7}{2}+$ to the 21 min ground state. In this case, the $\frac{7}{2}+$ state in silver must decay via unobserved low-spin states in cadmium to reach the spin $\frac{1}{2}+$ ground state of cadmium. Level systematics in this region indicate that the $d\frac{3}{2}+$ and perhaps the $d\frac{5}{2}+$ and $g\frac{7}{2}+$ levels in cadmium are involved. Closer investigation of the γ rays associated with ^{115}Ag and ^{115m}Ag decay is needed to resolve the level scheme.

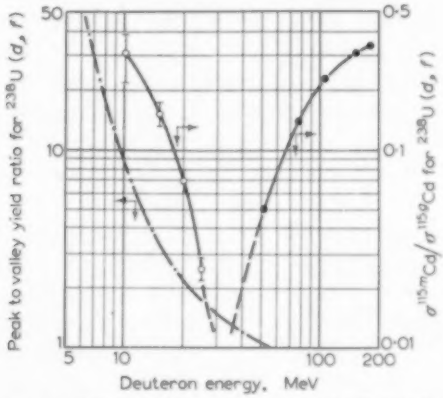


FIG. 1.—Isomer yield ratio of ^{115m}Cd($\frac{11}{2}-$) to ^{115g}Cd($\frac{1}{2}+$) for ^{238}U(d,f) (solid line), and peak to valley ratio for ^{238}U(d,f) (broken line) as a function of deuteron energy. ○ This paper; ● HICKS and GILBERT.[5]

WAHL and BONNER reported that 28 per cent of the mass 115 yield in thermal ^{235}U fission decays via ^{115m}Ag. The relative probabilities of primary formation of cadmium silver and palladium can be calculated from the charge distributions of PAPPAS[15] or STEINBERG and GLENDENIN[16] which differ in values of Z_A (most probable charge for a fragment of given mass) for regions near shell closures and in whether the fission neutrons are assumed to be emitted after or before fission respectively. Both calculations give similar magnitudes and show that for the reactions ^{235}U(n thermal, f) and to 25 MeV, ^{238}U(d,f), (d,nf), (d,2nf), (d,3nf) and (d,pf), the independent yields for ^{115}Cd are <1 per cent of the mass 115 chain yield, for ^{115}Ag yields 1–15 per cent, for ^{115}Pd 20–40 per cent and for mass 115 fragments further removed from stability 45–80 per cent of the chain yield. Thus in our experiments, even after correction for ^{115g}Ag effects, nearly all the observed ^{115g}Cd activity will be of chain yield origin via ^{115m}Ag, mostly resulting from the decay of palladium, rhodium, and more neutron rich primary fragments. Regardless of what spins are assigned to the ^{115}Ag levels, the ^{115g}Cd yield will not reflect spin population effects in fission strongly. Primary mass 115 fragments of all spins will on the average have many opportunities to adjust to the spin $\frac{1}{2}$ level of ^{115g}Cd as they decay by β- and γ-emission through levels in rhodium,

[14] C. D. CORYELL, U. SCHINDEWOLF and J. M. ALEXANDER, *Bull. Amer. Phys. Soc.* Ser. II, **3**, 207 (1958).
[15] A. C. PAPPAS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 19. United Nations, New York (1956).
[16] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 19. United Nations, New York (1956).

palladium and silver. Thus, the σ_m/σ_g ratio measured here is characteristic of σ (high-spin population)/σ(total-spin population) in the fissioning compound nucleus rather than σ(high-spin population)/σ(low-spin population).

The explanation behind the sharp minimum in the σ_m/σ_g curve in Fig. 1 is difficult to construct particularly in view of the present state of fission theory. TURKEVICH and NIDAY[17] made the proposal that the observed fission product mass distribution curves at low energies are a composite of two idealized curves, one corresponding to asymmetric and the other to symmetric fission. This has found experimental support in the work of SCHMITT and SUGARMAN[18] and in the results of a careful study by DAHL and PAPPAS.[19] The latter study revealed a slight peak in the minimum of the fission yield curve of ^{238}U with 31 MeV bremsstrahlung.

The recent experiments of JENSEN and FAIRHALL[20] on proton fission of radium have established quite definitely the existence of separate symmetric and asymmetric fission modes. The mass 115 chain in our work lies nearly at the bottom of the yield-mass curve "valley" and is characteristic of the symmetric fission mode. Over the energy interval studied in this work, the peak to valley ratio (Fig. 1) is falling rapidly as the yield for symmetric fission increases. We are then apparently in the trans-threshold region for symmetric fission. Assuming that σ^{115m}Cd/σ^{115g}Cd is influenced by the spin of the compound nucleus, our results seem to show that for low excitation energies, high-spin compound nuclei have a higher probability of penetrating the symmetric fission barrier than those of low spin. Such a possibility has been advanced by FONG.[21] Based on a suggestion by SWIATECKI,[22] PORILE[23] deduced a correlation between high orbital angular momentum of the fission fragments and increasing deformation energy (corresponding to a larger maximum radius for the saddle point configuration and hence closer approach to fission).

As the bombarding energy increases from 10–25 MeV, fissioning by low-spin compound nuclei begins to predominate. We suggest that the σ_m/σ_g ratio in this energy region depends on a factor of the form $(A_J'P_J')/(A_JP_J)$ where A_J' and A_J are proportional respectively to the abundance of high and low-spin compound nuclei among the total population and P_J' and P_J are the corresponding probabilities for fission barrier penetration. At low excitation energies, near the symmetric fission threshold, barrier penetration is the overwhelming consideration and favours high-spin modes. With increasing energy, all modes acquire significant barrier penetration and σ_m/σ_g falls reflecting the high proportion of low-spin compound nuclei expected at low excitation energies (see earlier discussion of results with tin, indium, and cadmium targets). As the excitation energy rises to 100 MeV and beyond (knock-on region), increased evaporation of particles and the higher orbital momentum carried in by the deuteron and out by protons overcoming the centrifugal barrier lead us to expect an increasing population of high spin compound nuclei. RUDSTAM[24] has shown that the average angular momentum of the residual nucleus increases with excitation energy. Other studies of independent yields of isomers in high energy

[17] A. TURKEVICH and J. B. NIDAY, *Phys. Rev.* **84**, 52 (1951).
[18] R. A. SCHMITT and N. SUGARMAN, *Phys. Rev.* **95**, 1260 (1954).
[19] J. B. DAHL and A. C. PAPPAS. To be published.
[20] R. C. JENSEN and A. W. FAIRHALL, *Phys. Rev.* **109**, 942 (1958).
[21] P. FONG, *Phys. Rev.* **102**, 434 (1956).
[22] W. J. SWIATECKI, *Phys. Rev.* **104**, 993 (1956).
[23] N. T. PORILE, *Phys. Rev.* **108**, 1526 (1957).
[24] G. RUDSTAM, *Spallation of Medium Elements*. Apelbergs Boktryckeri Ab., Uppsala (1956).

fission have shown the high-spin state to be favoured.[25] This trend causes the high-spin population term in the factor above to predominate and σ_m/σ_g increases with energy as observed. It is unfortunate that the interesting region embracing the minimum at 25–50 MeV in Fig. 1 is quite inaccessible to present deuteron accelerators, lying as it does above the range of AM cyclotrons and below that at which large FM machines can be operated conveniently. Perhaps a similar minimum in the σ_m/σ_g ratio will be observed in proton fission using one of the 100–150 MeV FM proton cyclotrons which can bridge the 10–100 MeV energy range.

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[25] P. KRUGER and N. SUGARMAN, *Phys. Rev.* **99**, 1459 (1955). W. F. BILLER, Report UCRL-2067 (1952), Unpublished.

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 183 to 197. Pergamon Press Ltd. Printed in Northern Ireland

RADIATIONS OF ^{93}Y AND ^{94}Y AND HALF-LIVES OF ^{93}Sr AND ^{94}Sr*

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Abstract—The radiations of ^{93}Y and ^{94}Y have been examined by β-ray spectrometry and γ-ray scintillation spectrometry. ^{93}Y decays about 90 per cent by a 2·89 ± 0·02-MeV β-transition to the ground state of ^{93}Zr; the spectrum of the 2·89 MeV group has a unique first-forbidden shape γ-rays of energies 0·267, 0·49, 0·665, 0·935, 1·15, 1·20, 1·42, 1·89–1·91, 2·14–2·18 and ~2·43 MeV accompany the remaining 10 per cent of the disintegrations. On the basis of γ–γ coincidence measurements, these radiations have been fitted to a partial decay scheme involving levels in ^{93}Zr at 0·267, 0·935, 1·42, 1·89, 2·18 and ~2·43 MeV.

^{94}Y has a complex β-spectrum of maximum energy 5·0 ± 0·2 MeV; the highest-energy group corresponds to the transition to the ground state of ^{94}Zr. The lower-energy β-transitions are accompanied by γ-rays of energies of 0·56, 0·92, 1·13, 1·65, 1·90, 2·13, 2·84 and 3·53 MeV, plus unresolved γ-ray groups at 2·57 and 3·06 MeV.

The half-lives of ^{93}Sr and ^{94}Sr, measured by experiments involving periodic chemical separations of ^{93}Y and ^{94}Y from fission-product strontium, are 8·2 ± 0·8 min and 1·3 ± 0·2 min, respectively. The half-lives of ^{93}Y and ^{94}Y are 10·25 ± 0·10 hr and 20 ± 1 min, respectively.

A search has been made for isomerism in ^{93}Y. Measurements on yttrium grown from fission-product strontium have shown no definite evidence for an isomer of ^{93}Y with a half-life in the range 30 sec to 3 hr. The yield of 10·25 hr ^{93}Y from fission of ^{235}U by water-moderated "pile" neutrons is (6·1 ± 0·6) per cent

ONE of the prominent yttrium fission-product activities is a 10 hr β-emitter, first observed by BALLOU[1] and, independently, by HAHN and STRASSMANN.[2] The maximum β-ray energy was given as 3·1 MeV on the basis of absorption measurements.[1] The assignment of this activity to ^{93}Y, proposed by other investigators[3,4] on the basis of β-decay energy and apparent absence of daughter zirconium activity, was later supported by fission-fragment range measurements.[5]

Recently, the radiations of the 10 hr ^{93}Y have been examined in detail by β- and γ-scintillation spectrometry by HEATH and VEGORS,[6] who formulated a decay scheme involving a predominant 3·1 MeV β-transition to the ^{93}Zr ground state and low-abundance β-transitions to ^{93}Zr levels at 0·265, 0·94, 1·40 and 2·14 MeV. These data are consistent with the assumption that the β-transitions proceed from a $p_{1/2}$ state of ^{93}Y.

A feature of interest is the possibility of isomerism in ^{93}Y. Both ^{89}Y and ^{91}Y

* Work performed under the auspices of the U.S. Atomic Energy Commission.
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(1) N. E. BALLOU, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record. Div. IV, Vol. 9, Paper 80. McGraw-Hill, New York (1951) This series reference will be abbreviated here after as NNES-PPR.
(2) O. HAHN and F. STRASSMANN, *Naturwissenshaften* **31**, 249 (1943); *Z. Physik* **121**, 729 (1943).
(3) B. SELIKSON and J. M. SIEGEL, NNES-PPR Vol. 9, Paper 81.
(4) L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, NNES-PPR Vol. 9, Paper 52.
(5) S. KATCOFF, J. A. MISKEL and C. W. STANLEY, *Phys. Rev.* 74, 631 (1948).
(6) R. L. HEATH and S. H. VEGORS, *Phys. Rev.* (to be published). See also R. L. HEATH, *Bull. Amer. Phys. Soc.* Series 2, **2**, 230 (1957).

have $p_{1/2}$ ground states, but a comparison of the trend in $p_{1/2}$–$g_{9/2}$ level spacings of the odd-mass yttrium isotopes with the corresponding trend in odd-mass niobium isotopes suggests that the ground state of ^{95}Y is likely to be $g_{9/2}$ and that the ground state of ^{93}Y could possibly be $g_{9/2}$. The decay of a $g_{9/2}$ state of ^{93}Y would depend on the relative position of its $p_{1/2}$ state and on the position of the lowest 7/2+ or 9/2+ excited state in ^{93}Zr. The evidence of direct β-transitions from the 10 hr ^{93}Y to the ^{93}Zr levels proposed by HEATH and VEGORS implies that these levels are all of spin $\leqslant 5/2$ and probably of even parity. On the other hand, the presence of a 7/2+ or 9/2+ level at 0·77 MeV in ^{95}Mo and of a 7/2+ level at 0·67 MeV in ^{97}Mo suggests that a similar level might exist at 1 MeV or less in ^{93}Zr. Such a level, if present, would not of course be populated to any measurable extent by β-decay from a $p_{1/2}$ state, but might be expected to appear, at least weakly, as a path for de-excitation of the ^{93}Zr states at 1·40 or 2·14 MeV if their spins were other than 1/2. If a 7/2+ level does exist within 1·5 MeV of the ground state of ^{93}Zr, a $g_{9/2}$ isomer of ^{93}Y would be expected to decay at least in part by an allowed β-transition with a half-life in the range 2–40 min. Moreover, if an isomeric transition in ^{93}Y, whether $p_{1/2} \rightarrow g_{9/2}$ or $g_{9/2} \rightarrow p_{1/2}$, were of energy $\leqslant 0{\cdot}2$ MeV, its competition with β-decay could be sufficiently weak to have escaped attention. From these qualitative considerations, it appeared worthwhile to search for an isomer of ^{93}Y which might previously have been over-looked.

The present paper describes a series of experiments on the formation and decay of ^{93}Y, with particular attention to the possibility of isomerism. In addition, since ^{94}Y is also present in rapidly-separated fission-product yttrium sources, an examination of the major features of its formation and decay is also described.

EXPERIMENTAL METHODS

Sample preparation

The yttrium sources used for measurements of half-life and radiations of ^{93}Y and ^{94}Y were obtained from ^{235}U which had been irradiated in the Los Alamos "Water Boiler" reactor. Yttrium was initially co-precipitated with LaF_3 or $La(OH)_3$. It was then further purified by additional fluoride precipitations, and was isolated carrier-free by passage of a solution of the sample in conc HCl through two anion-resin columns and a final elution from a cation-resin column with ammonium α-hydroxy*iso*butyrate.[7]

The half-lives of ^{93}Sr and ^{94}Sr were obtained from measurements of the relative amounts of the ^{93}Y and ^{94}Y components in the β-decay curves of a series of yttrium samples milked sequentially from fission-product strontium. The strontium (together with fission-product barium) was isolated from a solution of irradiated uranyl nitrate by precipitation of $Sr(NO_3)_2$ in the presence of yttrium hold-back carrier. The strontium was purified by a second $Sr(NO_3)_2$ precipitation in the presence of yttrium hold-back carrier, followed by two $Y(OH)_3$ scavenging precipitations. From this strontium (and barium) solution successive $Y(OH)_3$ precipitations were made at intervals corresponding to the previously-reported[8,9] approximate half-lives of ^{93}Sr and ^{94}Sr. The yttrium samples, dissolved in conc HNO_3, were purified by extraction into tributyl phosphate[9,10] (TBP), followed by washing of the TBP layer with conc HNO_3 and then back-extraction into water. This purification step served to separate yttrium from the lanthanum activities grown from barium decay. The yttrium samples were again precipitated as $Y(OH)_3$ and transferred to platinum plates, then dried and mounted for counting. The chemical yield of the hydroxide precipitation step was checked separately and found to be

[7] H. L. SMITH and D. C. HOFFMAN, *J. Inorg. Nucl. Chem.* **3**, 243 (1956).
[8] C. LIEBER, *Naturwissenshaften* **27**, 421 (1939).
[9] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 304 (1957).
[10] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).

$\geqslant$99 per cent. The relative over-all yields of the purification steps for each of the yttrium samples milked from the parent strontium were measured by reference to the amount of the 3·62 hr ^{92}Y component observed in each.

Instrumentation

The γ-ray spectra were measured with an unshielded 3 in. dia. × 3 in. thick NaI(Tl) crystal coupled to a 5 in. DuMont 6364 photomultiplier, used in conjunction with a non-overload linear amplifier and a fast 100-channel pulse-height analyser. For γ-γ coincidence work, a second scintillator unit with a 1½ in. dia. × 1½ in. thick NaI(Tl) crystal was used. The smaller crystal was positioned with its axis at right angles to the axis of the larger crystal; the faces of the larger and smaller crystals were about 4·5 cm and 2·0 cm, respectively, from the source, which was situated at the intersection of the crystal axes. Coincident events between selected photo-peak pulses from the small scintillator and any pulses from the large scintillator served to gate the pulse-height analyser, which then recorded the spectrum from the large crystal. The coincidence circuit had a resolving time of 0·5 μsec. Pieces of Lucite ¾ in. thick were placed over each scintillator to serve as β-ray absorbers.

The relative photo-peak efficiency function for the large crystal was taken from the detection efficiency curves of HEATH[11] and was converted to an absolute-efficiency curve for the present experimental arrangement by fitting to the measured photo-peak efficiencies of three 4π-counted γ-ray standards: ^{22}Na, ^{137}Cs, and ^{198}Au.

Two instruments were used for the measurement of electron spectra. The β-ray and internal-conversion electron spectra of ^{93}Y were measured with a ring-focus, solenoidal β-spectrometer patterned after the design of SCHMIDT.[12] The β-ray spectrum of ^{94}Y was measured with a 1½ in. dia. × 1½ in. thick transstilbene scintillator unit, used in conjunction with the electronic circuitry previously listed. The β-scintillation spectrometer was calibrated with the following sources: ^{24}Na, ^{32}P, ^{90}Sr–^{90}Y, ^{93}Y, ^{106}Ru–^{106}Rh, and ^{144}Ce–^{144}Pr.

EXPERIMENTAL RESULTS

Half-lives of ^{93}Y, ^{94}Y, ^{93}Sr *and* ^{94}Sr

The ^{93}Y half-life was measured on a set of three aliquots taken from a large sample which had been prepared for the observation of γ-scintillation spectra. The fission products were produced in an 8 min pile irradiation of ^{235}U, and the yttrium was removed at 8 min after the end of irradiation. The decay of all three samples was followed with β-proportional counters, and one of the samples was also counted on a γ-scintillation counter with its circuitry adjusted to accept pulses from all γ-rays above about 30 keV. The counts were continued until 12 days after the end of the irradiation, and the data, after subtraction of the small contribution of ^{91}Y, were submitted to least-squares analysis on an IBM 704 computer. The ^{93}Y β- and γ-half-lives agreed within 0·2 per cent; the average value was 10·25 hr, with an estimated error of 0·1 hr.

The ^{94}Y half-life was measured on two samples made up from a larger quantity of source material prepared for observation of β- and γ-scintillation spectra. In this case, the uranium was irradiated for 3·7 min and the first yttrium precipitation was performed 1·3 min after the end of irradiation. After purification, the half-life samples were counted on a β-proportional counter. The decay data are plotted in Fig. 1. Subtraction of the 10·25 hr ^{93}Y and 3·62 hr ^{92}Y components gave a strong 20 ± 1 min component, ^{94}Y, and at early times a small amount of a $\sim$9·5 min component which was attributed to ^{95}Y.

[11] R. L. HEATH, *Scintillation Spectrometry γ-Ray Spectrum Catalog* Phillips Petroleum Co. Atomic Energy Division Report IDO-16408 (July 1, 1957). (This report bears also the U.S. Department of Commerce designation TID-4500, Ed. 13, and is available from office of Technical Services, U.S. Department of Commerce, Washington 25, D.C.)

[12] F. H. SCHMIDT, *Rev. Sci. Instrum.* **23**, 361 (1952).

The ^{93}Sr half-life was obtained by measurement of the amount of the 10·25 hr ^{93}Y component in yttrium samples milked from fission-product strontium as described in the previous section. A sample of uranyl nitrate was irradiated for 7 min and final purification of the strontium was accomplished 30 min after the end of irradiation.

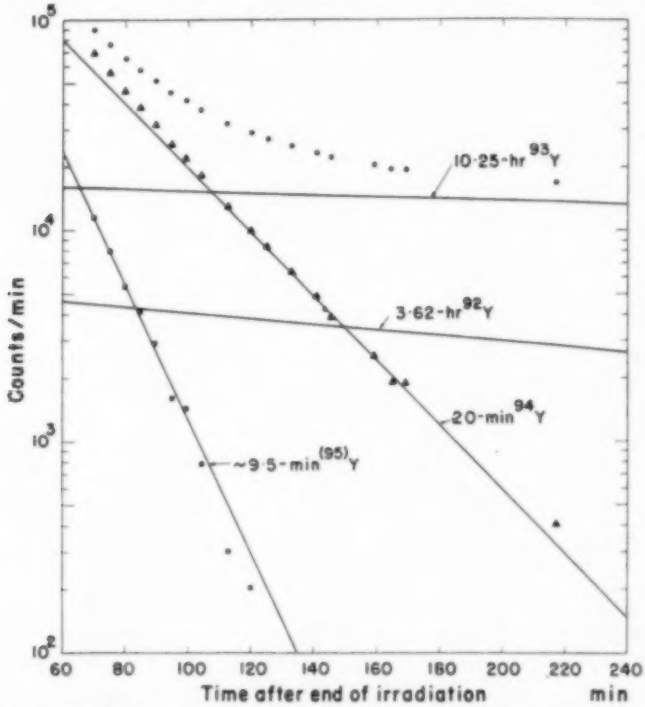

FIG. 1.—Partial β-decay curve of a fission-product yttrium sample prepared to optimise the ^{94}Y activity.

● Gross β-decay data.
▲ Points obtained after subtraction of 10·25 hr and 3·62 hr components.
■ Points obtained after subtraction of 10·25 hr, 3·62 hr and 20 min components.

Five successive yttrium milkings were performed at 7 min intervals. The ^{93}Y activities, after extrapolation back to the time of milking, are plotted in Fig. 2. The ^{93}Sr half-life obtained from these measurements was $8{\cdot}2 \pm 0{\cdot}8$ min.

The ^{94}Sr half-life was obtained in a similar manner; the strontium was purified 9·4 min after the end of a 2 min irradiation and four successive yttrium milkings were conducted at 2 min intervals. The ^{94}Y activities, extrapolated back to their respective separation times, are plotted in Fig. 3; the indicated ^{94}Sr half-life is $1{\cdot}3 \pm 0{\cdot}2$ min.

Radiations of ^{93}Y

The β-ray spectrum of ^{93}Y was measured on a source of estimated thickness 1 mg/cm², deposited from solution over a circle about 2·5 mm in diameter on a 0·83 mg/cm² aluminized Mylar backing. The observed momentum resolution was 1·1 per cent. The first few hours after preparation and mounting of the source, when the ^{92}Y content was still excessive, were employed in scanning for interval conversion

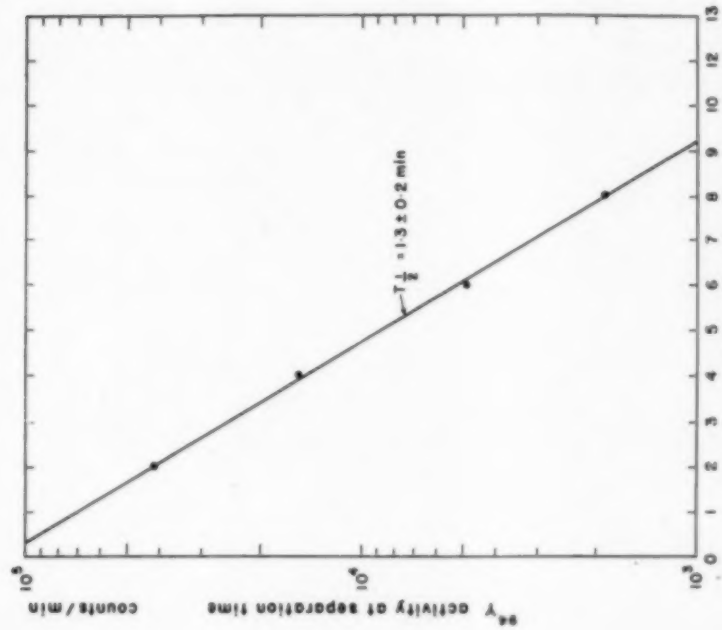

FIG. 3.—Decay curve of ^{94}Sr obtained by periodic separation of ^{94}Y.

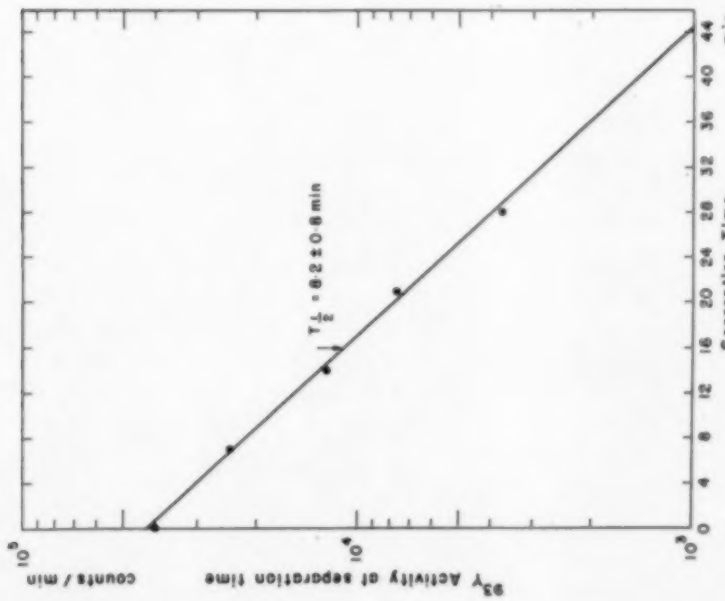

FIG. 2.—Decay curve of ^{93}Sr obtained by periodic separation of ^{93}Y.

electron lines. Measurement of the β-spectrum was begun approximately 23 hr after the end of the uranium irradiation, when the ^{92}Y β-decays comprised only about 4 per cent of the total.

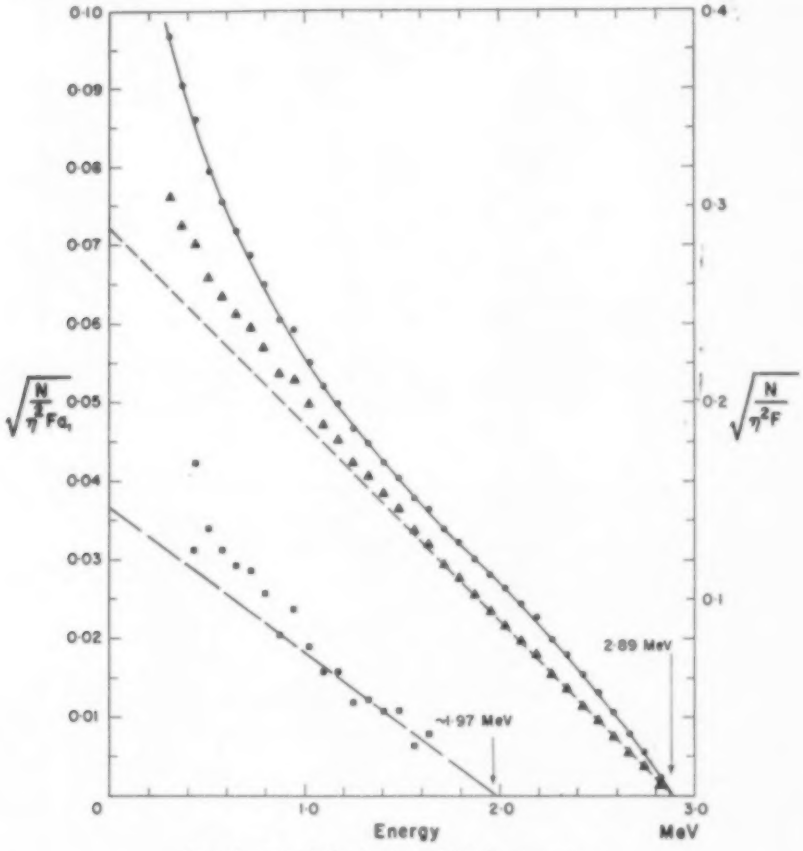

FIG. 4.—Fermi–Kurie plots of ^{93}Y β-ray spectrum.
● Uncorrected F–K plot (right-hand scale).
▲ F–K plot corrected by the $\Delta J = 2$ (yes) shape factor, $a_1 = q^2L_0 + 9L_1$ (left-hand scale).
■ Points resulting from subtraction of the principal group of the corrected plot.

The observed electron momentum distribution showed, in addition to the ^{93}Y β-continuum, peaks at 248·5 and 265 keV, corresponding to the K- and $(L + M)$-conversion electrons of a 267 $\pm$ 2 keV transition in zirconium. Comparison of the area of the K-conversion line with the area of the remainder of the β spectrum gave the intensity ratio: $N_{267K}/N_\beta = 1{\cdot}5_2 \times 10^{-3}$. A conventional Fermi–Kurie plot of the spectral data exhibited a convex curvature at the high-energy end. Correction of the β-energy distribution function by the $\Delta J = 2$ (yes) shape factor[13] $a_1 = q^2L_0 + 9L_1$ resulted in a linear plot with an end-point energy of 2·89 $\pm$ 0·02 MeV. The uncorrected and corrected plots are shown in Fig. 4. The departure from linearity in the region below about 1·7 MeV indicated the presence of weak β-groups at lower

[13] M. E. ROSE, C. L. PERRY and N. M. DISMUKE, Report ORNL-1459 Special (unpublished).

energies. A trial subtraction of the principal group yielded a set of points consistent with the presence of a second group with end-point energy about 1·97 MeV, but owing to its low abundance and to another factor to be described later, this and other possible low-energy groups could not be resolved in a quantitatively significant manner.

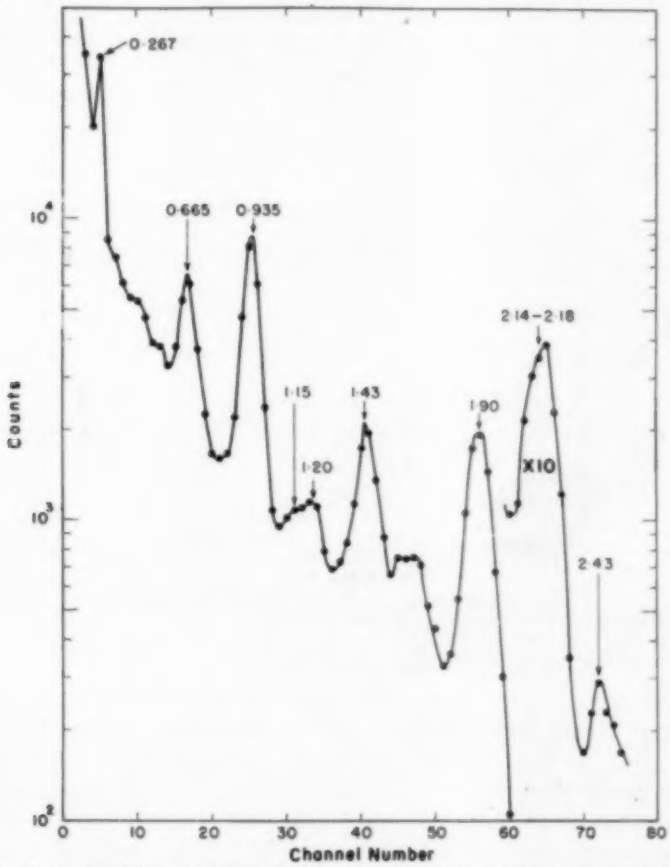

FIG. 5.—γ-scintillation spectrum of ^{93}Y, measured with 3 in. × 3 in. NaI(Tl) crystal. Photo-peak energies are given in MeV.

The γ-scintillation studies were performed on a sample of ^{93}Y source material, portions of which were also used for half-life determination. The scintillation measurements were begun about 26 hr after the end of the irradiation, when the ^{91}Y and ^{92}Y activities together constituted less than 1 per cent of the ^{93}Y activity. The disintegration rate of this source was determined by β-counting, at known efficiency, one of the other sources made up from the same preparation, and later comparing counting rates of the two sources. The β-counting efficiency was calculated by reference to an empirically-determined calibration curve relating counting efficiency to average β-energy,[14] and was estimated to be known to ± 5 per cent.

The γ-scintillation spectrum, plotted in Fig. 5, exhibited distinct photo-peaks at

[14] B. P. BAYHURST and R. J. PRESTWOOD, *Nucleonics* **17**, No. 3, 82 (1959).

$0{\cdot}267 \pm 0{\cdot}005$, $0{\cdot}665 \pm 0{\cdot}010$, $0{\cdot}935 \pm 0{\cdot}010$, $1{\cdot}43 \pm 0{\cdot}02$ and $1{\cdot}90 \pm 0{\cdot}02$ MeV, and a high-energy doublet which could be resolved graphically into peaks at $2{\cdot}14 \pm 0{\cdot}03$ and $2{\cdot}18 \pm 0{\cdot}03$ MeV. In addition, there was evidence of other photo-peaks near 2·5 MeV. There was no evidence for photo-peaks above this energy.

Additional information concerning the positions and populations of the excited states of ^{93}Zr produced by β-decay of ^{93}Y was obtained from a series of γ-γ coincidence measurements. The scintillation spectra gated by photo-peak pulses from the 0·267, 0·665 and 1·90 MeV γ-rays are plotted in Fig. 6.

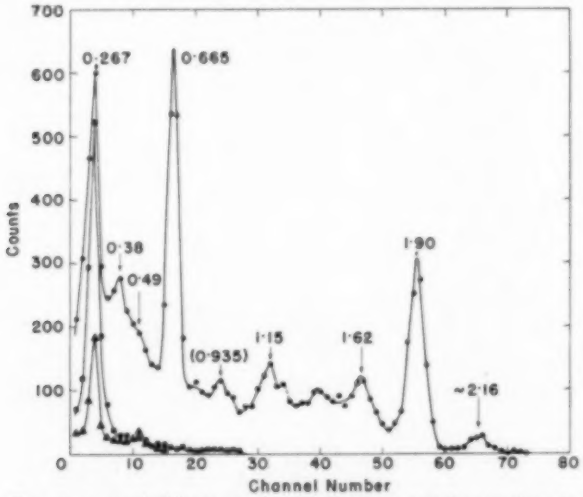

FIG. 6.—γ-γ coincidence spectra. Photo-peak energies are given in MeV.
● Spectrum gated by 0·267 MeV photo-peak pulses.
■ Spectrum gated by 0·665 MeV photo-peak pulses.
▲ Spectrum gated by 0·935 MeV photo-peak pulses.

The coincidence spectrum gated by the 0·267 MeV γ-pulses showed prominent peaks at the 0·267, 0·665, and 1·90 MeV positions, and weaker peaks at $0{\cdot}38 \pm 0{\cdot}02$, $1{\cdot}15 \pm 0{\cdot}03$, $1{\cdot}62 \pm 0{\cdot}03$ and $2{\cdot}16 \pm 0{\cdot}03$ MeV. In addition, the subtraction of cumulative Compton distributions in the region below 0·665 MeV revealed possibly another photo-peak at 0·49 MeV. The apparent photo-peak at ~1·39 MeV is the annihilation quantum escape peak from the 1·90 MeV γ-ray, and the peaks at the 0·267 and 0·935 MeV positions are undoubtedly due, in large part, to the corresponding photo-peak pulses which were coincident with bremsstrahlung and Compton pulses from higher-energy γ-rays included in the gate channel.

The coincidence spectrum gated by the 0·665 MeV photo-peak pulses exhibited an intense photo-peak at 0·267 MeV, plus indications of a considerably weaker one in the vicinity of 0·45 MeV. The spectrum gated by the 0·935 MeV photo-peak pulses had an intense photo-peak at the 0·267 MeV position and a weak peak at about 0·49 MeV. Neither spectrum showed measurable peaks above 0·7 MeV.

The γ-scintillation data from both the singles and coincidence measurements are summarized in Table 1. All γ-ray intensities are listed in terms of the intensity of the 0·935 MeV γ-ray, designated as 100. The intensities obtained directly from the photo-peaks of the singles spectrum are listed in the second column. Owing to the difficulty of measuring, in the singles spectrum, the intensities of some of the γ-rays observed

TABLE 1.—SUMMARY OF ^{93}Y γ-RAY DATA

γ-Ray energy (MeV)	Relative intensity		γ-Rays per 100 betas	Observed in coincidence with		
	from singles data	from 0·267 coincidence data		0·267	0·665	0·935
0·267 ± 0·002*	280 ± 25		6·4 ± 1·0	+†	+	+†
0·38 ± 0·02		1·2 ± 0·4	0·03 ± 0·01	+	?	?
0·49 ± 0·03		1·5 ± 0·5	$0{\cdot}03_4 \pm 0{\cdot}01_2$	+	?	+
0·665 ± 0·010	32 ± 6	32‡	0·7 ± 0·2	+	−	−
0·935 ± 0·010	100		2·3 ± 0·3	−†	−	−
1·15 ± 0·03		10 ± 2	0·23 ± 0·06	+	−	−
1·20 ± 0·03	7 ± 2		0·15 ± 0·05	?	−	−
1·42 ± 0·02	32 ± 6		0·7 ± 0·2	−	−	−
1·62 ± 0·03		3 ± 1	0·07 ± 0·03	+	−	−
1·90 ± 0·02	77 ± 8	70 ± 7	1·8 ± 0·3	+	−	−
2·14 ± 0·03	3 ± 1	5 ± 1	0·07 ± 0·03	+	−	−
2·18 ± 0·02	12 ± 3		0·27 ± 0·09			
2·43 ± 0·02	~2		~0·05	−	−	−

* Energy determined by β-spectrometry.

† Coincidences attributed to bremsstrahlung plus Compton scattering pulses in portion of spectrum selected as gate.

‡ Arbitrarily set at singles spectrum value.

clearly only in the 0·267 MeV-gated coincidence spectrum, these intensities were obtained indirectly. The procedure employed was the following: first, the intensities in the coincidence spectrum were measured and computed in terms of the intensity of the 0·665 MeV γ-ray; then, with the assumption that all of the 0·665 MeV γ-rays are in coincidence with the 0·267 MeV γ-rays, the relative intensities of the others were normalized to the value 32 attributed to the 0·665 MeV γ-ray in the singles spectrum. The results are tabulated in the third column. The areas of the 0·267, 0·665, and 1·90 MeV photo-peaks, as observed in the singles spectrum, were corrected for losses by accidental coincidence summing, which occurs whenever both γ-rays of a coincident pair enter the scintillation crystal together. This correction amounted to 1·2 per cent for the 0·267 MeV peak and 6 per cent for the peaks of γ-rays in coincidence with the 0·267 MeV γ-ray; in practical terms, the intensities of only the 0·665 and 1·90 MeV γ-rays were measurable with sufficient accuracy to justify application of the 6 per cent correction.

From the value of N_K/N_β obtained from the β-spectrometer measurements, together with N_γ/N_β derived from the γ-intensity measurements on sources of measured disintegration rate, the K-conversion coefficient of the 0·267 MeV transition was computed to be $2{\cdot}4 \times 10^{-2}$. The theoretical conversion coefficients for $E_\gamma = 0{\cdot}267$ MeV, $Z = 40$ are:[15,16] $E1$, $5{\cdot}9_6 \times 10^{-3}$; $E2$, $2{\cdot}83 \times 10^{-2}$; $M1$, $1{\cdot}31 \times 10^{-2}$; $M2$,

[15] L. A. SLIV and I. M. BAND, *Coefficients of Internal Conversion of γ-Radiation*, Part I *K*-Shell [Academy of Sciences of the U.S.S.R. Moscow-Leningrad (1956)] issued in the U.S.A. as Report 57 ICC Kl of the Physics Department, University of Illinois, Urbana, Illinois.

[16] M. E. ROSE, G. H. GOERTZEL and C. J. SWIFT, *Internal Conversion Coefficients* (privately circulated). For $E_\gamma = 0{\cdot}267$ MeV and $Z = 40$, the coefficients obtained by graphical interpolation from the tables of ROSE *et al.* agree with those obtained in a similar manner from the tables of SLIV and BAND, within graphing errors.

$6{\cdot}2 \times 10^{-2}$. The observed conversion coefficient is consistent with a 28% $M1$ + 72% $E2$ mixture.

The results of the β- and γ-radiation measurements permit the deduction of a number of features of the decay of the 10·25 hr ^{93}Y. The γ-ray data as summarized in Table 1 are consistent with the existence of excited states in ^{93}Zr at 0·267 ± 0·002, 0·935 ± 0·010, 1·42 ± 0·02, 1·89 ± 0·02 and 2·18 ± 0·02 MeV, plus probably others in the vicinity of 2·44 MeV. The low-intensity γ-rays at 0·38, 1·20, and 2·14 MeV could not be satisfactorily accounted for: the latter two could originate from weakly-

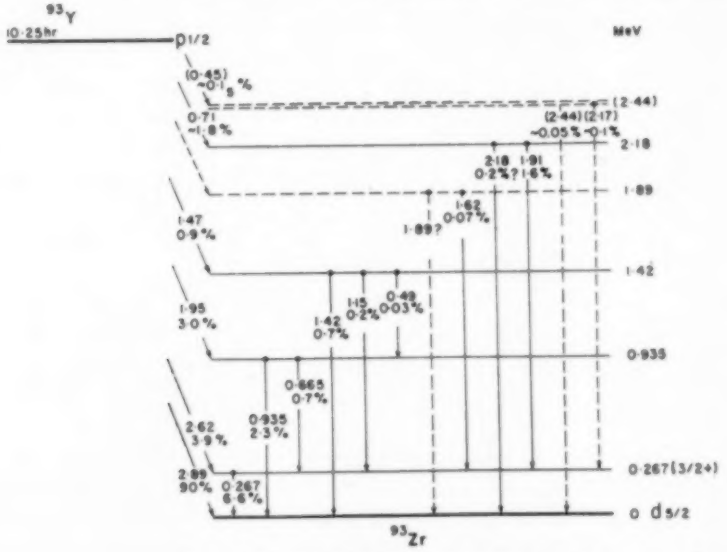

FIG. 7.—Decay scheme proposed for 10·25 hr ^{93}Y.

populated levels which de-excite predominantly to the ground state. This level structure, together with the level populations derived from the γ/β ratios of Table 1, were combined to give the decay scheme shown in Fig. 7. The abundances of the β-ray groups feeding the various states were deduced from the intensities of the γ-rays depopulating the states. The existence of a level at 1·89 MeV and of β-transitions feeding it cannot be definitely established from the present data; this level was postulated to account for the 1·62 MeV γ-transition observed in coincidence with the 0·267 MeV γ-transition, but the intensity of the transition direct to the ground state could not be computed because of masking by the more intense 1·91 MeV transition believed to proceed from the 2·18 MeV state.

With the assumption that the ground state of ^{93}Zr is $d_{5/2}$ (an assignment deduced from the mode of decay[17] of ^{93}Zr), the observation of the unique $\Delta J = 2$ (yes) shape in the spectrum of the ground-state β-transition from ^{93}Y establishes the spin and parity of the latter as 1/2−, or in single-particle terms, $p_{1/2}$. The log f_0t value for this β-transition is 7·8. The corrected comparative half-life, log f_1t, calculated in terms of the function given by DAVIDSON[18] for unique first-forbidden transitions, is 8·03,

[17] L. E. GLENDENIN and E. P. STEINBERG, Report ANL-5000 (1953). Unpublished.
[18] J. P. DAVIDSON, JR., *Phys. Rev.* **82**, 48 (1951).

where $f_1/f_0 = a(Z)(W_0^2 - 1) + b(Z)(W_0 - 1)$. The corresponding values for the similar unique transitions of ^{91}Sr and ^{91}Y are 8·27 and 8·52, respectively.

As may be seen from Fig. 4, the range over which the corrected Fermi–Kurie plot appears to be linear actually includes the first inner β-group as a "contaminant". However, graphical experiments involving the trial addition of a similar-in-energy second group to a pure-allowed spectrum showed that when the contribution of the β-"contaminant" was as much as 10 per cent, the change in shape of the high-energy end of the spectrum lay within the graphical plotting errors. The remaining β-groups were too numerous and too weak to be successfully resolved from the β-spectrometer data.

By analogy with the 0·203 MeV level of ^{95}Mo, identified by Coulomb excitation studies[19] as 3/2+, the 0·267 MeV level of ^{93}Zr may be tentatively designated also as 3/2+. This assignment is consistent with the computed $M1$–$E2$ mixture of the γ-transition to the ground state and with the type of level predicted for three equivalent 5/2 particles with weak coupling to the nuclear surface.[20]

Search for isomerism in ^{93}Y

The search for isomerism in ^{93}Y was guided by the considerations outlined in the introductory section. The study of the radiations of the 10·25 hr ^{93}Y had already yielded the following items of information relevant to the question of isomerism: (1) the shape of the β-spectrum established that the 10·25 hr ^{93}Y is a $p_{1/2}$ state; (2) the evidence of direct β-decay from this level to each of the excited states of ^{93}Zr, with the possible exception of the somewhat uncertain 1·89 MeV state, indicated that the excited states have spins $\leqslant 5/2$; (3) the absence of unaccounted-for internal conversion lines in the β-energy region above 0·035 MeV indicated that very little, if any, of the 10·25 hr ^{93}Y decays by isomeric transition to a lower state and that little of the 10·25 hr state could have been produced by isomeric transition from an upper state of comparable half-life; and (4) the low intensity of the γ-rays indicated that there could have been very little of a β-emitting $g_{9/2}$ isomeric state with a half-life in the vicinity of 10 hr. In addition, the β-decay curves of the yttrium samples which were measured in connection with the determination of the ^{93}Sr and ^{94}Sr half-lives by the milking technique exhibited only the half-life components 20 min, 3·6 hr, 10·25 hr and about 60 days, attributable to ^{94}Y, ^{92}Y, ^{93}Y and ^{91}Y, respectively.

A measurement of the fission yield of the 10·25 hr ^{93}Y offered another approach to the search for isomerism. The yield of ^{93}Zr from thermal neutron fission of ^{235}U has been cited[21] as $(6{\cdot}4_5 \pm \sim 0{\cdot}3)$ per cent, and the independent yields of ^{93}Zr and ^{93}Y are expected to be approximately 2×10^{-5} and $1{\cdot}7 \times 10^{-2}$, respectively, of the mass 93 chain yield.[17,22] Also, it has been observed that about 60 per cent of the decays of ^{91}Sr lead to the $g_{9/2}$ isomeric state of ^{91}Y,[23] and it would be expected that a comparable percentage of the ^{93}Sr decays should lead to a $g_{9/2}$ state of ^{93}Y. Hence, the existence of a $g_{9/2}$ isomeric state of ^{93}Y through which a part of the mass 93 chain is diverted could result in observation of an anomalous fission yield for the 10·25 hr ^{93}Y.

[19] F. K. McGowan and P. H. Stelson, *Phys. Rev.* **109**, 901 (1958).
[20] K. W. Ford and C. Levinson, *Phys. Rev.* **100**, 1 (1955).
[21] L. E. Glendenin, E. P. Steinberg, K. F. Flynn, R. J. Hayden and M. G. Inghram, results cited by E. P. Steinberg and L. E. Glendenin, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 3. United Nations (1956).
[22] A. C. Pappas, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 19. United Nations (1956).
[23] D. P. Ames, M. E. Bunker, L. M. Langer and B. M. Sorensen, *Phys. Rev.* **91**, 68 (1953).

A piece of enriched ^{235}U foil wrapped in aluminium was irradiated for 2 min at the edge of the spherical core of the reactor. The uranium and aluminium were dissolved together and duplicate analyses for yttrium and molybdenum were performed. The β-decay of the yttrium samples was followed for 20 days and the data were submitted to a least-squares analysis with 58·8 day (^{91}Y), 64·4 hr (^{90}Y), 10·25 hr (^{93}Y) and 3·62 hr (^{92}Y) half-lives specified. The number of atoms of ^{93}Y produced was calculated from the activity of the 10·25 hr component corrected for chemical yield, counting efficiency,[14] growth from an 8·2 min predecessor, and decay of the latter during irradiation. The number of fissions was determined by analysis and measurement of ^{99}Mo. This 66·4 hr β-emitter is the radiochemical reference standard used at this Laboratory, and the empirical ratio K = fissions/^{99}Mo activity is redetermined from time to time by radiochemical analysis of ^{235}U samples in which the number of fissions has been determined by comparison fission counting.

The ^{93}Y fission-yield values obtained for the two samples were both 6·11 per cent. With estimated uncertainties of 7 per cent in the number of ^{93}Y atoms and 3 per cent in the number of fissions, the fission yield was taken to be (6·11 $\pm$ 0·6) per cent. Comparison of this value with a fission yield of (6·45 $\pm$ 0·3) per cent for ^{93}Zr shows that not more than $\sim$20 per cent of the decay of the ^{93}Sr could have by-passed the 10·25 hr ^{93}Y.

The most probable possibility remaining for isomerism in ^{93}Y appeared to be that of a short-lived upper state which decays by isomeric transition to the 10·25 hr state. This possibility was explored by experiments involving rapid isolation and counting of yttrium grown from fission-product strontium. Two experiments, covering different half-life ranges, were performed. In the first, the strontium was isolated and three yttrium milkings were performed, starting 30 min after the end of irradiation. Each of the three yttrium samples was purified and then β-counted over a period of 12 hr; in addition, γ-spectra were observed from time to time in the intervals between the β-counts. The β-decay curves contained no measurable amount of any component shorter than 3·6 hr, and the γ-spectra exhibited only the characteristic peaks of ^{92}Y, plus the 0·55 MeV peak of ^{91m}Y. From these data and from the timing of the separations and measurements, it was concluded that no appreciable amount of any new β- or γ-emitting species of half-life greater than about 15 min was produced. The half-life range up to 15 min was covered by a similar experiment in which the strontium clean-up steps were completed 10 min after the end of irradiation and the yttrium was milked at 3 min intervals by precipitation. Although counting was started on the yttrium samples within 1 min after removal from the parent strontium solution, neither β- nor γ-counts showed any evidence for components with half-lives in the range from $\sim$0·5 to 20 min.

The foregoing data constitute evidence for the absence in ^{93}Y of a simple $g_{9/2}$–$p_{1/2}$ isomeric pair as is encountered in ^{87}Y, ^{89}Y, and ^{91}Y. They indicate, instead, that there may exist an intermediate level of intermediate spin. This level could be 3/2- or possibly 5/2-; either one, with plausible energy spacings, could result in an isomeric transition half-life less than 0·5 min.

Radiations of ^{94}Y

The β-ray spectrum of ^{94}Y was measured by scintillation spectrometry on a source prepared so as to maximize the $^{94}Y/^{93}Y$ activity ratio. The sample was

prepared by evaporation from carrier-free solution onto an aluminium plate 0·063 in. thick. Several spectra were measured, over the time span from 1 hr to 3 hr after the end of the uranium irradiation. The scintillation β-spectrum had an end-point of $5{\cdot}0 \pm 0{\cdot}2$ MeV.

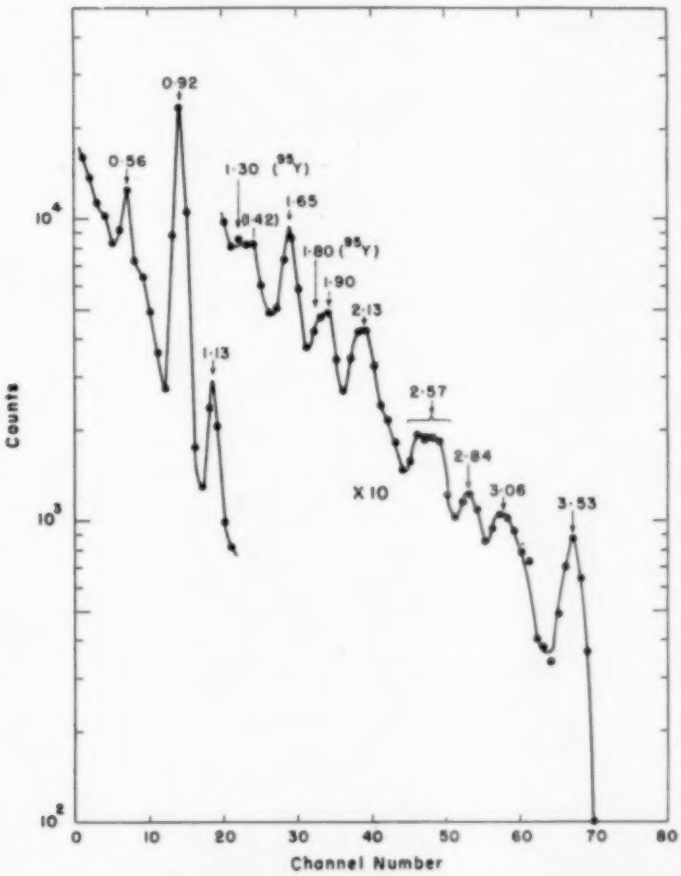

FIG. 8.—γ-scintillation spectrum of ^{94}Y, measured with 3 in. × 3 in. NaI(Tl) crystal. Photo-peak energies are given in MeV.

The γ-spectrum measurements were performed on a second source made up from the same preparation. Its absolute β-disintegration rate was determined by later comparison with a third source which had been counted at known efficiency on the standard β-proportional counter. The γ-scintillation spectra were observed at approximately half-hour intervals from 1 hr to 7 hr, and again at 18·5 hr after the uranium irradiation, so that the radiations of the other fission-product yttrium isotopes could be distinguished from those of ^{94}Y. The spectrum observed at 78 min is shown in Fig. 8. The photo-peaks at 0·92, 1·13, 1·65, 1·90, 2·13, 2·57, 2·84, 3·06 and 3·53 MeV decayed with a half-life of approximately 20 min and were assigned to ^{94}Y. In addition, the 0·56 MeV peak contained a 20 min component sufficiently strong to provide assurance that it was due, in major part, to ^{94}Y rather than to the small amount of

^{91m}Y also present in the preparation. Evidence was found also for contributions from γ-rays at about 1·30 and 1·80 MeV which decayed with a half-life considerably shorter than 20 min; these γ-rays were provisionally assigned to the 10 min ^{95}Y,

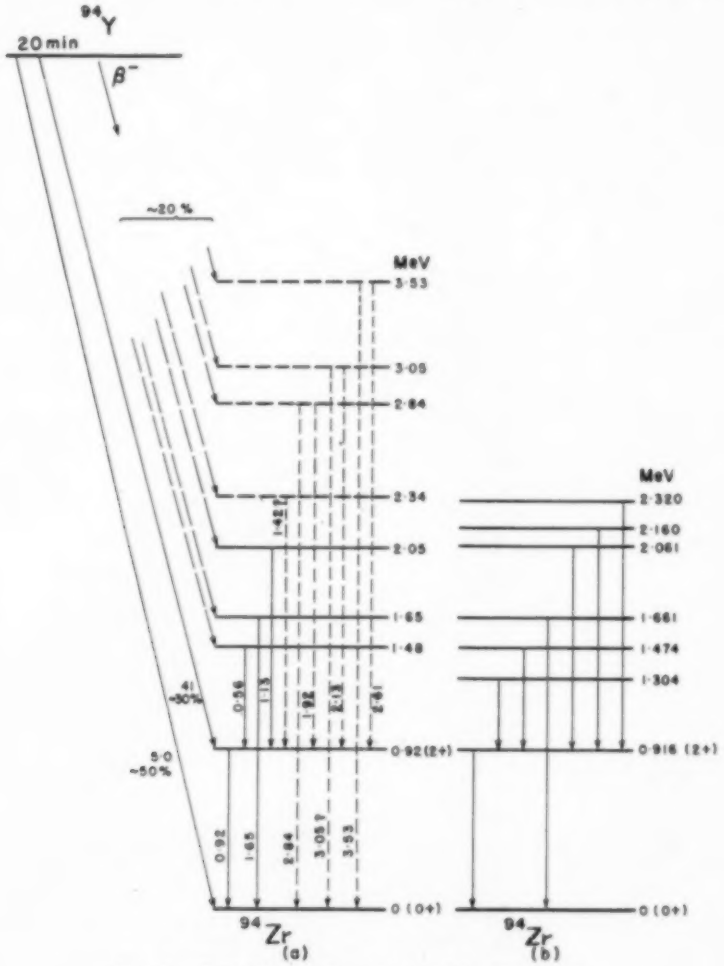

FIG. 9.—Partial decay scheme proposed for 20 min ^{94}Y.
(a) ^{94}Zr levels populated in beta decay of ^{94}Y, as deduced from γ-ray data
(b) ^{94}Zr level scheme from neutron inelastic scattering measurements.[34]

which was evident in small amount in the early β-counts on this preparation. The γ-ray data are summarized in Table 2.

Although the preliminary data recorded in Table 2 indicate that the ^{94}Y γ-ray spectrum is rather complex, they do permit some useful conclusions. First, the relative strength of the 0·92 MeV γ-ray suggests that the level from which it proceeds is fed at least half by β-decay, and that this level is probably the first excited state of ^{94}Zr. Second, the γ/β ratios listed in the third column of the table add up to only 65/100, showing that at least 35 per cent of the ^{94}Y β-transitions proceed directly to

the ^{94}Zr ground state, and hence that the observed maximum β-ray energy, 5·0 ± 0·2 MeV, is the Q_β for the ^{94}Y → ^{94}Zr decay.

Recent information on the level structure and γ-transitions in ^{94}Zr obtained by neutron inelastic scattering measurements[24] offers a useful guide for the interpretation of some of the ^{94}Y decay data. Fig. 9 shows the ^{94}Zr level scheme deduced from the above-mentioned work, together with a partial decay scheme of ^{94}Y formulated

TABLE 2.—SUMMARY OF ^{94}Y γ-RAY DATA

γ-Ray energy (MeV)	Relative intensity	γ-Rays per 100 betas
0·56 ± 0·01	13	6
0·92 ± 0·01	100	43
1·13 ± 0·02	11	5
1·65 ± 0·02	5·7	2·4
1·90 ± 0·03	3·8	1·6
2·13 ± 0·03	5·6	2·4
2·57 (doublet)	3·4	1·5
2·84 ± 0·03	1·6	0·7
3·06 (doublet?)	3	1·3
3·53 ± 0·03	2·5	1·1
1·42?	—	—

by fitting in the γ-ray energies and intensities from Table 2. It is noteworthy that at least four of the first seven excited states of ^{94}Zr appear to be populated by decay of ^{94}Y. Also, although there is insufficient information for the determination of the positions and populations of the ^{94}Zr levels at higher energies, reasonable estimates may be made of the fractions of the total ^{94}Y β-transitions proceeding to the ground state and first excited state of ^{94}Zr. In particular, it may be deduced that about 50 per cent of the β-transitions proceed to the ^{94}Zr ground state, and hence that the log f_0t and log f_1t values for the ground state β-transitions are $7{\cdot}5_6$ and $8{\cdot}2_9$, respectively. The log f_1t values for the ground-state β-transitions ^{90}Y → ^{90}Zr and ^{92}Y → ^{92}Zr are 8·09 and 8·24, respectively. The similarity in the log f_1t values suggests that the ground state of ^{94}Y, may also, like those of ^{90}Y and ^{92}Y, be 2−.

Acknowledgements—The authors wish to acknowledge the co-operation of the group at the Los Alamos Water Boiler Reactor in providing the irradiations. Thanks are also due to Mrs. F. LAWRENCE, Mr. D. GILCHRIST and Mr. R. CHAVEZ for assistance with the chemistry and treatment of the data.

[24] R. B. DAY and D. A. LIND. Private communication.

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 198 to 204. Pergamon Press Ltd. Printed in Northern Ireland

γ-RAYS FOLLOWING THE β-DECAY OF RARE-EARTH α-EMITTERS*

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Abstract—The β-decay properties of the rare-earth α-emitters, ^{150}Dy, ^{151}Dy, ^{152}Dy and ^{149}Tb, are discussed. By bombardment of stable praseodymium with ^{14}N ions at different energies in the Berkeley heavy-ion linear accelerator the three dysprosium isotopes have been produced. γ-spectra have been obtained and the following γ-rays have been assigned to the decay of the three nuclides, 390 keV (^{150}Dy), 145 keV (^{151}Dy) and 255 keV (^{152}Dy). Annihilation peaks have been observed to decay with the half-lives of the three isotopes, indicating that the nuclides must emit positrons. In addition, the mass assignments of ^{150}Dy and ^{151}Dy, the 8 min and 19 min dysprosium α-emitters respectively, have been determined with certainty. ^{149}Tb has been produced by bombarding stable praseodymium with ^{12}C ions. The energies of the γ-rays following the decay of ^{149}Tb are 170, 230, 360 and 640 keV.

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IN a recent publication we discussed the α-emitting properties of a number of rare earth isotopes.[1] The nuclides discussed included, in addition to previously known activities ^{150}Dy, ^{151}Dy, ^{152}Dy, ^{149}Tb and ^{151}Tb, two new α-emitters ^{153}Dy and ^{154}Dy.

From the estimated α-half-lives it is evident that these isotopes not only decay by the emission of α-particles but also should be β-unstable. With the exception of ^{151}Tb the β-decay properties of these isotopes had never been studied. Consequently, an attempt was made to determine the α-branching ratios of ^{152}Dy and ^{153}Dy and to identify some γ-rays following their β-decays. The two nuclides were produced by bombarding enriched ^{152}Gd with 48 MeV helium ions in the Berkeley 60 in. cyclotron. The dysprosium fraction was isolated by a separation method described previously.[1] The presence of ^{152}Dy and ^{153}Dy in the dysprosium fraction was established by studying the α-particles emitted in the decay of the two isotopes. The γ-spectrum of the sample was also obtained. The decay curve of the K X-ray peak yielded no 2·5 hr (^{152}Dy) or 5 hr (^{153}Dy) components. The shortest half-life seen was about 9 hr, believed to be a composite of an 8·2 hr (^{157}Dy) half-life and a new 10 hr (^{155}Dy) activity. None of the photon peaks exhibited a 2·5 hr or 5 hr half-life. Our inability to see either of the two activities was very probably due to the fact that they were both obscured by the large quantities of ^{155}Dy and ^{157}Dy present in the sample. The latter two isotopes are the chief products in α-particle bombardments on gadolinium enriched in ^{152}Gd because of the large amounts of ^{154}Gd, ^{155}Gd, ^{156}Gd and ^{157}Gd present in the target material. Even the use of higher-energy helium ions does not prevent the formation of ^{155}Dy and ^{157}Dy from the numerous stable isotopes of gadolinium.

To study the β-decay properties of the dysprosium α-emitters (with mass numbers

* This work was performed under the auspices of the U.S. Atomic Energy Commission.
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[1] K. S. TOTH and J. O. RASMUSSEN, *Phys. Rev.* **109**, 121 (1958).

between and including 150 and 154) these extremely neutron-deficient isotopes have to be produced free of the interfering ^{155}Dy and ^{157}Dy. The use of heavy bombarding particles—specifically nitrogen ions—solves the problem. Nitrogen ions impinging on natural monoisotopic praseodymium (mass number 141) form the compound nucleus, ^{155}Dy. This unstable intermediate then posseses sufficient energy to boil off at least several neutrons, thus forming the dysprosium α-emitters with no ^{155}Dy or ^{157}Dy. By the use of ^{12}C ions on praseodymium ^{149}Tb has been produced and its β-decay properties have been studied, free of the less neutron-deficient terbium isotopes.

Recently the heavy-ion linear accelerator has come into operation at the University of California Radiation Laboratory, facilitating the studies herein described.

EXPERIMENTAL METHOD

The accelerator imparts an energy of 10 MeV for each nucleon making up the accelerated particle. Thus ^{14}N ions are accelerated to 140 MeV. The target assembly used necessitated the interposition of two aluminium foils between the beam and the target material. The thicknesses of the foils were varied and three ^{14}N bombarding energies were employed. The energies were approximately 110, 80, and 35 MeV, according to BARRETT's range-energy curves of ^{14}N ions in aluminium.[2] At the lowest bombarding energy, the heaviest product seen was ^{152}Dy, while at the highest bombarding energy evidence of the (N, 7n) reaction was observed. ^{149}Tb was produced in a 65 MeV ^{12}C bombardment.

In most of the experiments no chemical separations were attempted. Rather, the targets (praseodymium oxide powder) were counted directly so that the short-lived products such as the 7 min ^{150}Dy and the 19 min ^{151}Dy could be seen. The chemical separations were not especially necessary since the dysprosium isotopes could be identified by following their decay by means of α-particle counters. Once the isotopes present in the samples had been determined, the same half-lives could be looked for among the peaks observed in the γ-spectra that were being obtained at the same time as the α-counting was proceeding. A 100 channel γ-pulse-height analyser was employed to obtain the γ-ray spectra. The analyser is used with a scintillation counter with a 3 in. × 3 in. NaI(Tl) crystal.

The γ-rays of ^{150}Dy, ^{151}Dy, ^{152}Dy

In order that the presentation of our results may be somewhat clearer the previously determined half-lives of the isotopes entering into the discussion are listed:

(a) ^{150}Dy	8 min
(b) ^{151}Dy	19 min
(c) ^{152}Dy	2·5 hr
(d) ^{149}Tb	4 hr

In the two bombardments using 35 and 80 MeV nitrogen ions the following experimental procedure was employed. In each case the target material was divided into two samples. Within 10 min of the termination of the bombardment both the samples, in each experiment, were counted. One sample was counted in an α-counter while simultaneously the second sample was γ-analysed by use of the 100 channel pulse-height analyser. The α-counter decay curve was then resolved into its components and the half-lives present in the sample were determined in this manner. The half-lives seen in the two α-decay curves were

35 MeV: 19 min, 2·5 hr, and some longer-lived activity;

80 MeV: 8 min, 4 hr, and possibly some 19 min activity, which may have caused the nonlinearity of the later decay points in the 8 min component after the 4 hr one had been subtracted out.

From the above decay curves it was thus learned that (a) ^{151}Dy and ^{152}Dy were present in the 35 MeV bombardment and that (b) ^{150}Dy, ^{149}Tb and possibly some ^{151}Dy were present in the 80 MeV bombardment.

The γ-spectrum obtained in the 35 MeV experiment approximately 10 min after bombardment time is shown in Fig. 1. The spectrum taken with the same sample 5 hr later is shown in Fig. 2. In the

[2] R. J. BARRETT, *Calculated Range-Energy Curves for Heavy Ions* (unpublished), UCRL, Berkeley (1957).

first spectrum the most prominent peak, excluding the *K* X-ray and annihilation peaks, is at 145 keV. At the later time this particular γ-ray has disappeared. A 255 keV γ-ray, which in the first diagram appears only as a small peak, is now the most intense one (again excluding the *K* X-ray and annihilation peaks). The half-life of the 145 keV γ-ray was found to be about 25 min. The 255 keV γ-ray

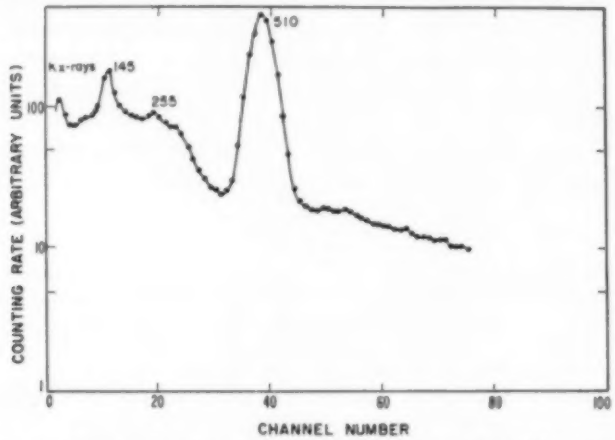

Fig. 1.—γ-spectrum taken 10 min after termination of the 35 MeV ^{14}N bombardment on ^{141}Pr. Energies of peaks are indicated in keV.

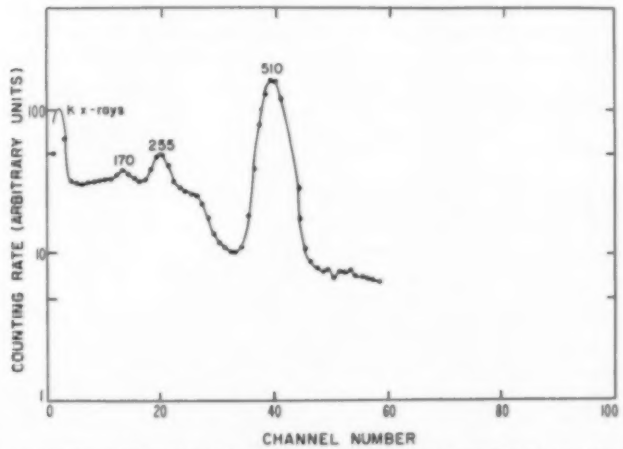

Fig. 2.—γ-spectrum taken 5 hr after completion of the 35 MeV ^{14}N bombardment on ^{141}Pr. Energies of peaks are indicated keV.

diminished in intensity with a 2·5 hr half-life. The two γ-rays, 145 and 255 keV, evidently follow the decay of ^{151}Dy and ^{153}Dy respectively.

Figs. 3 and 4 show the γ-spectra obtained in the 80 MeV bombardment, where the first one was taken approximately 10 min after bombardment time and the second about 40 min after the first. An intense γ-ray is seen at the earlier time at 390 keV. Forty minutes later the γ-ray has essentially disappeared. The half-life of the 390 keV peak was determined and found to be about 8 min. The γ-ray thus seems to follow the decay of the 8 min dysprosium α-emitter.

The γ-ray following the decay of ^{151}Dy has an energy of 145 keV and represents a transition in ^{151}Tb. It is interesting to note that a nucleus with the same number of neutrons (86) as ^{151}Tb, ^{149}Eu, has a level at 150 keV.[3] This level depopulates to the ground state of ^{149}Eu by the emission of a γ-ray

[3] V. S. Shirley, W. G. Smith and J. O. Rasmussen, *Nucl. Phys.* **4**, 395 (1957).

of the same energy.' The γ-ray is the most prominent one seen in the decay of ^{145}Gd to ^{149}Eu. It seems quite possible that the 145 keV γ-ray seen in the decay of ^{151}Dy may also represent a transition from the first excited state to the ground level of ^{151}Tb.

The decay curves obtained from the annihilation peaks in the two bombardments indicated the

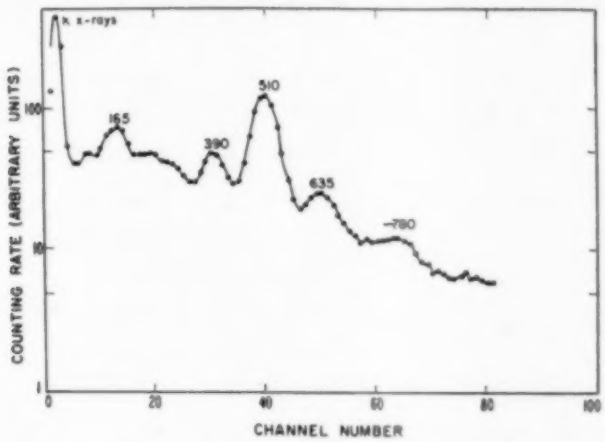

FIG. 3.—γ-spectrum taken 10 min after completion of the 80 MeV ^{14}N bombardment on ^{141}Pr. Energies of peaks are indicated in keV.

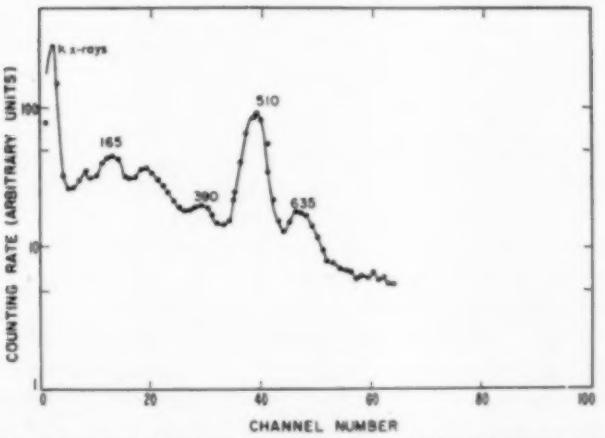

FIG. 4.—γ-spectrum taken 50 min after termination of the 80 MeV ^{14}N bombardment of ^{141}Pr. Energies of peaks are indicated in keV.

presence of components with the half-lives of the three dysprosium α-emitters discussed in this section. Thus all three of them, ^{150}Dy, ^{151}Dy and ^{152}Dy, must emit positrons. The α-branching ratios of the three isotopes were not determined because the samples were thick, as a result of which their true α-disintegration-rates were not determinable.

The assignment of mass numbers to ^{150}Dy *and* ^{151}Dy

In the publication on rare-earth α-emitters[1] it was stated that the 8 min and 19 min dysprosium α-emitters were almost certainly ^{150}Dy and ^{151}Dy respectively, for the following reasons:

(a) The 2·5 hr dysprosium α-emitter had been assigned a mass number of 152.

(b) A new isotope had been found which was probably ^{149}Dy.

(c) From the first two facts it followed that the 8 min and 19 min activities must have mass numbers between 150 and 152.

(d) Because a higher decay energy usually belongs to a lighter nucleus (for the same atomic number) the 8 min activity with an α-decay energy of 4·2 MeV was logically ^{150}Dy, and the 19 min activity with an α-decay energy of 4·06 MeV was ^{151}Dy.

Up to now in our discussion we have assumed the mass assignments to be correct. The evidence in this work is sufficiently clear to make the mass assignments a certainty.

The 8 min activity, as identified by the α-particles it emits, was observed in greatest relative abundance in the 80 MeV bombardments when compared with the abundance of the α-particles from the 4 hr ^{149}Tb. A γ-ray with the same half-life was also observed in the same experiment. The α-activity due to this isotope was seen in much less abundance in the 110 MeV bombardment, again when compared with the α-activity due to ^{149}Tb. The γ-ray was also identified at this energy (see Fig. 5) but again in much less abundance. The half-life was not identified in the 35 MeV bombardment either by its α-particles or by the γ-ray. α-activity with a 19 min half-life was seen clearly at the 35 MeV bombardment. A γ-ray was also observed that decayed with the same half-life. At 80 MeV there was a possibility that the 19 min activity may have been seen in the α-decay curve. However, the γ-ray assigned to the isotope was absent in the γ-spectrum. The evidence clearly demonstrates that the 8 min activity has a lower mass number than does the 19 min nuclide.

That the 8 min activity appeared in less abundance (relative to the 4 hr ^{149}Tb) at 110 MeV than at 80 MeV indicates that the mass number of the 8 min activity has to be greater than 149. Summing the available information and representing the mass number of the isotopes by A, we have

(a) A of the 19 min isotope $>$ A of the 8 min isotope $>$ 149,

(b) from the previous work, A of the 19 min isotope is less than 152.

Therefore, the 8 min activity must be ^{150}Dy, and the 19 min activity must be ^{151}Dy.

Results of the 110 MeV *bombardment*

The experiment at this energy was performed three times. The results in all three cases were in essential agreement. Because the only α-emitter seen in this case was ^{149}Tb, it was difficult to make assignments as unambiguously as was done in the previous section. However, some conclusions can be drawn and these are presented below.

From the α-counter decay curve we were able to determine approximately with what half-life ^{149}Tb grew in from ^{149}Dy. The half-life found in this case was closer to 20 min than to the 8 min half-life reported for ^{149}Dy by us previously.[1] One thing is certain, ^{149}Dy has been seen and its half-life is on the order of 10 or 20 min.

Fig. 5 is the γ-spectrum taken approximately 10 min after the termination of the 110 MeV bombardment. The differences between Figs. 3 and 5 are apparent. First, the 390 keV γ-ray of ^{150}Dy decay is in much less abundance at the higher energy (Fig. 5). Second, the 780 keV gamma, assigned to ^{148}Tb decay in some recent work,[4] has increased in intensity in Fig. 5. Third, a γ-ray at 300 keV has appeared in Fig. 5 which was absent in Fig. 3. The half-life of the 300 keV peak was found to be between 18 and 25 min. The γ-rays at 165 and 635 keV have been found to belong to ^{149}Tb decay. The two appear in approximately the same intensities in both the spectra, indicating that ^{149}Tb (initially ^{149}Dy) must be produced in about equal amounts at the two bombarding energies. In addition to the 4 hr component in the decay curve of the 165 keV peak, there was a shorter component with a half-life of about 16 min. The decay curve of the 510 keV peak yielded an activity of about 20 min plus the 1 hr activity of ^{148}Tb.

It is difficult to determine whether the 165 keV γ-ray really does have a shorter-lived component or whether the short half-life is due only to the Compton background underneath. If the component is real, it would be logical to assign it to ^{149}Dy, because

[4] K. S. Toth and J. O. Rasmussen, UCRL-8374; to be published in this journal.

the relative intensity of the 165 keV peak seems not to change appreciably at the two bombarding energies (80 and 110 MeV), rather than to an isotope with a greater or smaller mass number. This is done because the same is true of the 635 keV γ-ray which is known to belong definitely to ^{149}Tb. The latter γ-ray has only the 4 hr component. Using the opposite argument, the 300 keV γ-ray should be assigned to

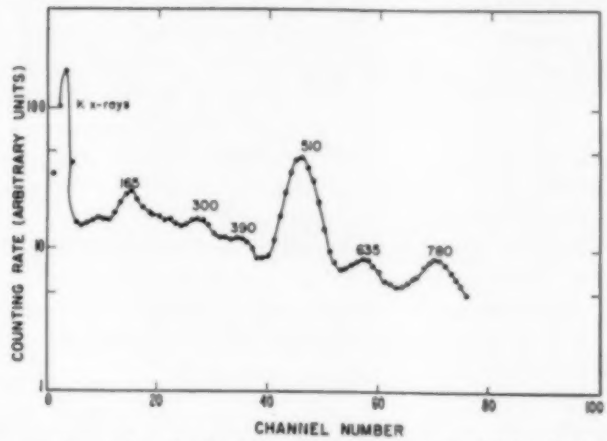

FIG. 5.—γ-spectrum taken 10 min after completion of the 110 MeV bombardment on ^{141}Pr. Energies of peaks are indicated in keV.

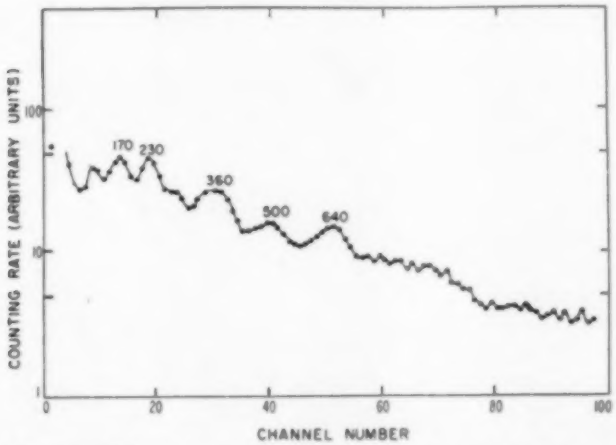

FIG. 6.—The γ-ray of the spectrum of ^{149}Tb, an activity produced in a 65 MeV ^{12}C bombardment on ^{141}Pr. Energies of peaks are indicated in keV.

some isotope with a mass number smaller than 149 since it appears only in the 110 MeV bombardment. What dysprosium or terbium isotope it belongs to is difficult to say. Also, it is impossible to say to what isotope the short-lived component of the 510 keV peak belongs.

The γ-rays of ^{149}Tb

The target material obtained from the 65 MeV ^{12}C bombardment was chemically purified by means of an ion-exchange method described previously.[1] The terbium

fraction was then studied. By the use of an α-counter the 4 hr ^{149}Tb was shown to be present in the terbium fraction. The γ-ray spectrum was obtained; it is shown in Fig. 6. The spectrum was taken after all of the ^{148}Tb mentioned previously[4] had decayed. The half-life of ^{148}Tb has been found to be approximately 70 min, so that it was necessary only to wait long enough to be certain that the 70 min activity was no longer present. The spectrum was taken soon enough after chemical separation, however, so that only a small amount, if any, of the 9 day ^{149}Gd was present. The half-lives of the peaks shown in Fig. 6 were found to be 4 hr. The energies of the γ-rays assigned to the decay of ^{149}Tb are 170, 230, 360 and 640 keV. There is also a peak at approximately 500 keV, which may be either the annihilation peak due to positrons or a γ-ray of that energy. According to previous workers,[5] ^{149}Tb does not emit positrons, but the observation was not sufficiently quantitative to enable us to decide about the existence of a 500 keV nuclear gamma.

The α-branching ratio of ^{149}Tb has been determined recently by Winsberg[6] using a 4π γ-scintillation detector. He quotes a figure of 10 ± 2 per cent for the ratio $\alpha/(EC + \alpha)$. The decay scheme of ^{149}Tb has not been determined. A large number of γ-rays do seem to follow the decay of ^{149}Tb indicating that the disintegration scheme of ^{149}Tb must be rather complex.

Acknowledgements—We should like to acknowledge the help and co-operation of the crew of the Berkeley heavy-ion linear accelerator. The assistance of the Health Chemistry Department of the Radiation Laboratory in monitoring and target transportation is also appreciated.

[5] J. O. Rasmussen, S. G. Thompson and A. Ghiorso, *Phys. Rev.* **89**, 33 (1953).
[6] L. Winsberg UCRL-3958, Abstract for the American Physical Society Meeting, December (1958).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 205 to 214. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONEGATIVITIES CALCULATED USING A MODIFICATION OF PAULING'S EQUATION*

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Abstract—An equation for calculating the electronegativity of an element is developed from Pauling's relationship between the extra-ionic resonance energy and the electronegativity differences in which the bond energy of a metal-metal single bond need not be known nor any assumptions need be made concerning it. From this relationship the electronegativity of fifty-four elements has been calculated. In addition, electronegativities of different oxidation states of six elements have been calculated. A brief discussion concerning the possibility of alternation of electronegativities in Groups IV B and V B is presented.

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IN a comprehensive review of the electronegativity concept, PRITCHARD and SKINNER[1] pointed out that only fourteen of the thirty-three electronegativities of elements calculated by Pauling were obtained using his relationship between the extra-ionic resonance energy (Δ) and electronegativity differences ($x_X - x_M$). Pauling's equation is

$$23{\cdot}06\,|x_X - x_M|^2 = B(\text{M–X}) - \tfrac{1}{2}[B(\text{M–M}) + B(\text{X–X})] \qquad (1)$$

in which B(M–X) is the average bond energy between the atoms within the parentheses. In applying this equation, it is essential that the same orbital of atom M is involved in both the M–M bond and M–X bond. One of the serious difficulties in employing the above equation, particularly for metals, is the evaluation of the bond energy of the metal–metal single bond involving the same orbital as in the M–X bond. Another difficulty is the evaluation of the M–X average bond energy from the symmetrical MX_n compound which exists as a solid. In order to calculate B(M–X), the latent heat of sublimation for the compound must be known, but unfortunately there are many compounds for which this property has not been measured.

For many cases in which there was insufficient data to use equation (1), Pauling approximated Δ by dividing the negative of the heat of formation of the solid compound by n, the number of symmetrical bonds. If this is done, the assumption[1] is made implicitly that

$$B(\text{M–M}) = \frac{2}{n}[L_s(\text{M}) - L_s(\text{MX}_n)] \qquad (2)$$

where L_s(M) is the heat of sublimation of the metal and $L_s(MX_n)$ is the heat of sublimation of MX_n, which certainly is not an obvious one. Furthermore, this cannot be true for all MX_n compounds for a given metal atom, otherwise all such compounds would have to have identical heats of sublimation.

If in some way Pauling's relationship could be altered so that the above defects were absent, a more reliable set of electronegativities could be calculated.

* This work was supported in part by the U.S.A.E.C. under Contract AT(30-1)-1670.

[1] H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1955).

There has been a growing discontent among some inorganic chemists[2,3] because Pauling's electronegativity scale did not reveal alternations with increasing atomic number in certain groups of elements. For example, ROCHOW and ALLRED[2] and SANDERSON[3] both claim that the order of electronegativities of the elements in Group IV B should be C > Pb > Ge > Sn > Si and not the expected order of decreasing x with increasing atomic number. Using the most recent thermochemical data and assuming the bond energy of M–M is one-half the heat of atomization of the element from a tetrahedral lattice, ROCHOW and ALLRED[2] were able to obtain an alternation in the electronegativity of the elements of Group IV B, using Pauling's equation. In addition to the electronegativities calculated from thermochemical data, they presented electronegativity values from chemical shifts of nuclear magnetic resonance, nuclear quadrupole coupling constants, electrostatic potentials, electrostatic forces and work functions which strongly support the alternation hypothesis for Group IV B.

It would be of interest to establish whether the alternation of electronegativity of elements in the several groups shows up using a derived expression from Pauling's equation in which no assumptions are necessary.

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A MODIFICATION OF PAULING'S ELECTRONEGATIVITY EXPRESSION

As far as the authors are aware, no one has considered determining the electronegativity of an element M (especially a metal) by using equation (1) for two different symmetrical compounds such as MX_n and MY_n and then subtracting one from the other. Since the electronegativities of hydrogen and the halogens have been evaluated from many different compounds,[4] and since they form compounds of the MX_n type with almost all the elements, they will be considered as either the X or Y in the compounds above. On subtracting the two relationships of equation (1) the result is

$$23{\cdot}06\{|x_X - x_M|^2 - |x_Y - x_M|^2\} = [B(M\text{–}X) - \tfrac{1}{2}B(X\text{–}X)] - [B(M\text{–}Y) - \tfrac{1}{2}B(Y\text{–}Y)] \quad (3)$$

It should be noted that the controversial bond energy of M–M single bond has been cancelled out. This expression is easily transformed to give x_M directly

$$x_M = \left[\frac{x_X + x_Y}{2}\right] - \left\{\frac{[B(M\text{–}X) - \tfrac{1}{2}B(X\text{–}X)] - [B(M\text{–}Y) - \tfrac{1}{2}B(Y\text{–}Y)]}{2(23{\cdot}06)(x_X - x_Y)}\right\} \quad (4)$$

Although one could employ equation (4) directly if the bond energies of the various bonds were tabulated, it will be more profitable for us to substitute the expressions for bond energies in terms of observable thermochemical data.

The bond energy of M–X can be evaluated for a symmetrical molecule MX_n in terms of the heat of formation of MX_n ($\Delta H_f(MX_n)$). Assuming the standard state of M is a solid, X_2 is a solid, and MX_n is a solid, the heat of formation of the solid is given by

$$\Delta H_f(MX_n)_s = L_s(M) + \left(\frac{n}{2}\right) L_s(X_2) + \left(\frac{n}{2}\right) B(X_2) - Q_a(MX_n) - L_s(MX_n) \quad (5)$$

[2] E. G. ROCHOW and A. L. ALLRED, *J. Inorg. Nucl. Chem.* **5**, 269 (1958).
[3] R. T. SANDERSON, *J. Amer. Chem. Soc.* **74**, 4792 (1952).
[4] M. L. HUGGINS, *J. Amer. Chem. Soc.* **75**, 4123 (1953).

in which $Q_a(MX_n)$ is the heat of atomization of the molecule MX_n. The heat of atomization is the energy needed to remove all the atoms in their ground states to infinity from the molecule in its ground state. The bond energy is defined as 1/*nth* of the heat of atomization for a symmetrical molecule of the type MX_n,

i.e. $$B(\mathrm{M\text{–}X}) = \frac{Q_a(\mathrm{MX}_n)}{n}.$$

From the definition of bond energy and equation (5), one can show that the expression for the electronegativity of M in equation (4) can be written as

$$x_M = \left[\frac{x_X + x_Y}{2}\right] - \left\{\frac{-[\Delta H_f(MX_n)_g - \Delta H_f(MY_n)_g] - [L_s(MX_n) - L_s(MY_n)] + \left(\frac{n}{2}\right)[L_s(X_2) - L_s(Y_2)]}{2(23{\cdot}06)n(x_X - x_Y)}\right\} \tag{6}$$

In case both X_2 and Y_2 are gases in their standard states and MX_n and MY_n are both gases in their standard states, the numerator of the second term on the right hand side is just the negative of the differences in the heat of formation of the gases. Under these conditions equation (6) can be rewritten

$$x_M = \frac{x_X + x_Y}{2} - \left\{-\frac{[\Delta H_f(MX_n)_g - \Delta H_f(MY_n)_g]}{2(23{\cdot}06)n(x_X - x_Y)}\right\} \tag{7}$$

One other important situation may arise in evaluating x_M by equation (6), and that s that in many cases the heat of formation of the solid compounds are known but not the latent heats of sublimation of these compounds. In such cases the only assumption needed is that the latent heats of sublimation of the two closely allied compounds (two different halides of the same element M) are equal. From some available data, the error to be expected in the numerator of equation (6) because of this assumption should not be more than about 8 kcal/mole. However, if the crystal structure or the molecular structure of the two halides of the same metal M are different, the difference in their heats of sublimation may be quite large and, therefore, the electronegativity of the element calculated would be in error.

An advantage of equation (6) or (7) over that of Pauling's expression [equation (1)] is that a value for the bond energy of the M–M single bond is not needed and, furthermore, no assumption as to the orbitals used in the M–M and M–X bond need be made. Another advantage is that the electronegativity of the element M can be calculated directly from thermochemical data (heats of formation of compounds, latent heats of sublimation and evaporation) which are readily available without having to make the unlikely assumption concerning B(M–M) as expressed in equation (2). In order to evaluate B(M–X), (which is needed in Pauling's equation) a value for the latent heat of sublimation of the element must be known, which for many elements has not been determined accurately.

On the other hand, in order to use equation (6) or (7) the difference in electronegativities of X and Y must be known very precisely. For a small error in $(x_X - x_Y)$

may be a large relative error, if the difference itself is small. This situation could result in a large error in the second term on the right in equation (6) or (7). Fortunately, the second term is usually less than 40 per cent of the first so that the relative error in the final result will be, in most cases, much less than two-thirds the relative error in $(x_X - x_Y)$.

RESULTS OF CALCULATIONS

The electronegativity values were calculated using either equation (6) or (7) for as many elements as possible. Only hydrides, fluorides, chlorides, bromides and iodides were used as the MX_n compounds. Since the values of electronegativity differences $(x_X - x_Y)$ are so critical, the most accurate electronegativity values calculated for hydrogen and the halogens by HUGGINS[4] from the most recent thermochemical data available were used in the present calculations. His values based on $x_H = 2{\cdot}20$ in units of $(eV)^{\frac{1}{2}}$ are fluorine 3·90, chlorine 3·15, bromine 2·95 and iodine 2·65. The thermochemical data were taken from *Selected Values of Chemical Thermodynamics*.[5]

The calculations were carried out for all possible pairs of the hydrides and the halides for Groups IV B, V B, and VI B. However, for the transition metals and those in Groups I A, II A and III B the hydrides were not employed.

The results of the calculations are given in Table 1. Following the elements listed in the first column are the mean values of the electronegativities calculated from the number of pairs which is tabulated in the next column. If the electronegativities could be calculated from heats of formation of gases, and the heats of formation of liquid (or solid), both sets of data are given in adjacent columns. For elements which have several stable oxidation states, the data are first tabulated for that oxidation state which corresponds to its group number. Below these values are given the data for as many of the other stable oxidation states as could be determined. In the next to the last column are given our best value of the electronegativity of the element in its valence state corresponding to its group number. Whenever the electronegativities could be calculated from the heats of formation of the gaseous compounds, those values were considered the best. In the final column are given those published by Pauling. It should be kept in mind that our scale is based on $x_H = 2{\cdot}20$ and so might be 0·10 unit greater than Pauling's values.

The electronegativity values for each of the alkali metals calculated by using all the possible pair combinations of the alkali halides showed very poor agreement among themselves. One would expect poor agreement if, for at least one of the halides involved, Pauling's original equation failed. That Pauling's equation does not apply for alkali halides (and hydrides) was stressed by PRITCHARD and SKINNER.[1] In fact, PAULING[7] himself recognized that his method of calculation would not apply "in case that $(x_A - x_B)$ is very large" although he did not elaborate on this point. GORDY,[8] and DAILEY and TOWNES[9] have correlated the per cent ionic character in diatomic molecules to the electronegativity differences between the two atoms. Even though the two relationships differ somewhat, both correlations show that if the electronegativity difference is greater than 1·6, the ionic character is greater than 85 per cent, and at

[5] F. D. ROSSINI, *Selected Values of Chemical Thermodynamic Properties*. Circular 500 N.B.S. Government Printing Office, Washington, D.C. (1952).
[6] These are values reported by M. HAISSINSKY, *J. Phys. Rad.* **7**, 7 (1946).
[7] L. PAULING, *The Nature of the Chemical Bond* p. 61. Cornell University Press, New York (1942).
[8] W. GORDY, *Microwave Spectroscopy*. John Wiley, New York (1953).
[9] B. P. DAILEY and C. H. TOWNES, *J. Chem. Phys.* **23**, 118 (1955).

TABLE 1.—ELECTRONEGATIVITIES CALCULATED FROM THE MODIFIED PAULING EQUATION AND COMPARED TO PAULING'S

Group	Average electronegativity values calculated from $MX_n(p)$*				Our best values‡	PAULING'S values
H					2·20	2·1
VII B	(These are HUGGINS' values)					
F					3·90	4·0
Cl					3·15	3·0
Br					2·95	2·8
I					2·65	2·4
VI B	$MX_2(g)$	No.†				
O	3·45	3			3·45	3·5
S					—	2·5
Se	2·34	1			2·34	2·4
Te					—	2·1
V B	$MX_3(g)$	No.	$MX_3(l)$	No.		
N	2·98	1			2·98	3·0
P	2·19	3	2·24	1	2·19	2·1
As	1·97	3	2·20	2	1·97	2·0
Sb			2·28	1	2·28	1·8
Bi					—	—
IV B	$MX_4(g)$	No.	$MX_4(l)$	No.		
C	2·57	6			2·57	2·5
Si	1·90	10	1·88	1	1·90	1·8
Ge	2·02	3	2·05	1	2·02	1·7
Sn	—	—	2·47	1	2·47	1·7
Pb	—	—			—	—
	$MX_2(s)$	No.				
Sn	2·18	3			—	—
Pb	2·30	6			—	—
III B	$MX_3(g)$	No.	$MX_3(s)$	No.		
B	1·64	1			1·64	2·0
Al			2·00	6	2·00	1·5
Ga			2·16	3	2·16	1·6[a]
In			2·18	3	2·18	1·6[a]
Tl			2·55	1	2·55	1·5[a]
II A	$MX_2(g)$	No.				
Be	1·66	3			1·66	1·5
Mg	1·77	3			1·77	1·2
Ca	1·87	3			1·87	1·0
Sr	1·88	3			1·88	1·0
Ba	1·91	3			1·91	0·9

TABLE 1.—(*continued*)

Group	Average electronegativity values calculated from $MX_n(p)$*				Our best values‡‡	PAULING'S values
I A	No consistent values calculated for alkali metals.					
I B	MX(*g*)	No.	MX(*s*)	No.		
Cu	1·34	1	—		1·34	1·80[6]
Ag	—		2·54	3	2·54	1·8[6]
Au			2·87	3	2·87	2·3[6]
II B	$MX_2(s)$	No.				
Zn	2·17	3			2·17	1·5[6]
Cd	2·37	6			2·37	1·5[6]
Hg	2·57	3			2·57	1·9[6]
III A	$MX_3(s)$	No.				
Sc	1·95	1			1·95	1·3
Y	1·90	1			1·90	1·3
La	1·84	1			1·84	—
IV A	$MX_4(s)$	No.				
Ti	2·22	3			2·22	1·6
Zr	2·10	6			2·10	1·6
Hf	—	—			—	—
	$MX_3(s)$	No.	$MX_2(s)$	No.		
Ti	2·05	6	2·20	6		
Zr	2·12	6	2·14	6		
Hf	—	—	—	—		
V A	No data on V, Nb, and Ta				—	—
VI A	$MX_6(s)$	No.				
Cr	—	—			—	2·1[6]
Mo	—	—			—	—
W	2·46	1			2·46	—
	$MX_5(s)$	No.	$MX_4(s)$	No.		
Cr	—	—	—	—		
Mo	2·59	3	2·53	3		
W	2·29	3	2·35	3		
	$MX_2(s)$	No.	$MX_3(s)$	No.		
Cr	2·27	1	2·31	3		
Mo	2·48	3	2·54	3		
W	—	—	2·42	3		

TABLE 1.—(*continued*)

Group	Average electronegativity values calculated from $MX_n(p)$*		Our best values‡	PAULING's values
VII A	$MX_2(s)$	No.		
Mn	2·20	6	2·20	1·4[6]
VIII	$MX_2(s)$	No.		
Fe	2·13	3	2·13	1·65[6]
Co	2·19	6	2·19	1·7[6]
Ni	2·13	6	2·13	1·7[6]
Pd	2·34	1	2·34	2·0[6]
Pt	2·78	3	2·78	2·1[6]
Lanthanides				
	$MX_3(s)$	No.		
Ce	1·84	1	1·84	—
Pr	1·84	1	1·84	—
Nd	1·84	1	1·84	—
Sm	1·83	1	1·83	—
Gd	1·81	1	1·81	—
Dy	1·87	1	1·87	—
Ho	1·76	1	1·76	—
Er	1·90	1	1·90	—
Tm	1·90	1	1·90	—
Lu	1·85	1	1·85	—
Actinides				
	$MX_4(s)$	No.		
Th	1·59	3	1·59	—
U	1·89	3	1·89	—
	$MX_3(s)$	No.		
Np	1·85	3	1·85	—
Pu	1·83	3	1·83	—

* The letter in parentheses indicates state of matter of the compounds used in calculation: gas (*g*), liquid (*l*), solid (*s*).
† In the No. column is given the number of pairs of values used in calculating the averages.
‡ "Our Best Value" is taken from the gaseous data whenever possible.

2·0 there exists practically 100 per cent ionic character. Since the Δ in Pauling's equation is a measure of the *extra-ionic* resonance energy, one might expect the breakdown of Pauling's equation when the ionicity of the bond approaches 100 per cent. Naturally, if Pauling's relationship is invalidated for bonds with a great deal of ionic character, so will any deduction from it such as equations (6) and (7).

Assuming that if the electronegativity difference was 1·8 or greater (90–100 per cent ionic character) equations (6) and (7) would not be valid, one could decide which halides of an element may or may not be used to evaluate the electronegativity of that element. For example, any element whose electronegativity was less than 2·1 could

not be evaluated using its fluoride, for the electronegativity difference would be greater than 1·8. In Table 2 are listed the electronegativities of the halogens and hydrogen and also the minimum electronegativity an element can have in order to evaluate it using that particular halide or hydride.

Using Table 2 for the minimum values of electronegativities, a procedure for accepting or rejecting a value calculated from equation (6) or (7) was established. Having calculated the electronegativity of an element from as many pairs of halides and hydrides as possible, the smallest value obtained from either the Br–I or I–H pair

TABLE 2.—THE MINIMUM ELECTRONEGATIVITY AN ELEMENT MUST POSSESS IN ORDER TO CALCULATE ITS ELECTRONEGATIVITY FROM THE CORRESPONDING HALIDES AND HYDRIDES IN EQUATION (6)

Halogen	$x_{Hal.}$	Minimum x of element
F	3·90	2·1
Cl	3·15	1·3
Br	2·95	1·1
I	2·65	0·8
H	2·20	0·4

was noted. If this smallest value was 2·1 or larger and the maximum spread between the largest and smallest values was less than 0·4 $(eV)^{\frac{1}{2}}$, all the results were used for averaging. On the other hand if the smallest value was between 1·3 and 2·1, no values obtained from pairs having a fluoride were used. Again the average was calculated if the spread of the remaining values was less than 0·4 $(eV)^{\frac{1}{2}}$. Results obtained from pairs with either chlorides or fluorides were discarded if the electronegativity was between 1·1 and 1·3. Finally, if the electronegativity was between 0·8 to 1·1, no values calculated from bromides, chlorides or fluorides were accepted.

The hydrides were used for calculating electronegativities of elements in only Groups IV B, V B, and VI B. This decision was made because very divergent values were obtained by Pauling himself with his original equations for the alkali metals and because the transition metals form interstitial hydrides, whose properties are more intimately related to their crystal structure rather than molecular structure.

The electronegativities of the halogens listed are those of HUGGINS. On the other hand, no acceptable values were calculated according to the above criterion for the alkali metals.

Before discussing any conclusions drawn from the data in Table 1, it might be wise to consider the types and magnitude of errors one might expect for these values. For those calculations in which the assumption that the latent heat of sublimation of two halides of metal M (having similar crystal and molecular structures) are equal, we estimate that they may be in error of the order of 0·1 to 0·2 $(eV)^{\frac{1}{2}}$. Since, we accepted a small spread when calculating the average electronegativity values, mean

deviations up to 0·13 $(eV)^{\frac{1}{2}}$ were obtained. Because of these two factors, the calculated electronegativities of some metals may be good to only 0·2 or 0·3 $(eV)^{\frac{1}{2}}$. If, as was pointed out above, the crystal or molecular structures of the two halides employed in a given calculation were quite different larger errors would be expected.

CONCLUSIONS

Except for germanium, tin and antimony the electronegativity values calculated for the elements in Groups IV B, V B, and VI B agree reasonably well with those of PAULING and (though not tabulated) agree well with values of HUGGINS. Our value for Ge agrees within 0·02 units with that of ROCHOW and ALLRED.[2]

In several cases, the electronegativity of an element was calculated from the heats of formation of gaseous MX_n and from the heats of formation of the liquid compound. In the latter case the assumption is made that the heats of vaporization of two similar halides are equal. The agreement between the two values was always better than 15 per cent. The x_M calculated from gaseous data, which is the more accurate, was, in some cases, less than and in others greater than the result from the liquid data. While it would have been instructive to be able to say that all the electronegativity values calculated from liquid or solid data were always too high (or all too low), the above results prevent us from making any such generalizations.

The electronegativity values for the alkaline earths are from 0·6 to 1·0 $(eV)^{\frac{1}{2}}$ units larger than those of PAULING's. Furthermore, in our case they increase slightly as the atomic number increases rather than decrease. The same is true for Group III B. These results are not what one might expect from, say, chemical evidence. However, taking into account the errors associated with the electronegativity values, and in the case of boron, the fact that only one value could be calculated, the slight divergence in the order of electronegativities in Groups II A and III B is probably not too significant. In addition to the above, errors in electronegativity values in Group III B may have crept in because the halides of some members of this group may have different crystal or molecular structures, as for example, aluminium chloride and aluminium bromide.

Unfortunately there is not sufficient information to calculate reliable electronegativity values for the elements in any group of the periodic table all with the same valence. For this reason no conclusive statement can be formulated concerning the alternation of electronegativities of elements in a given group as the atomic number increases. In Group V B, the electronegativity decreases from N to P to As and then increases with Sb. Since no x for Bi was calculated, one cannot say whether there is alternation in this group. In Group IV B the electronegativity decreases from C to Si and increases slightly at Ge and more at Sn. Although there is a minimum x value, one cannot definitely say there is alternation. While our results afford no proof of the alternation of electronegativities in Groups IV B and V B, they do not contradict the possibility of alternation. On the other hand, if one considers the excellent agreement between the present electronegativity values for C(2·57), Si(1·90) and Ge(2·02) with those of ROCHOW and ALLRED (2·60, 1·90 and 2·00 $(eV)^{\frac{1}{2}}$ respectively) and the fact that the electronegativity of Sn was calculated from only one pair of solid halides, it does seem likely that alternation of electronegativities occurs in Group IV B.

The electronegativity of the transition elements in their highest oxidation state have been tabulated in column 6 of Table 1. In most cases our results are 0·6 to 0·7

units larger than that given by PAULING. The agreement would have been better by 0·1 $(eV)^{\frac{1}{2}}$ if both of us had chosen x_H to be the same. Our results show that the transition elements in their highest oxidation states are about as electronegative as hydrogen, and considerably more than the alkali metals and somewhat more electronegative than the alkaline earth metals.

For those elements which have more than one oxidation number, the electronegativities were calculated for each of the element's valences. In most cases the electronegativity for the several oxidation states of an element agreed within 7 per cent (see Ti, Zr, Cr, Mo, W). It would appear that the electronegativity of an element defined by Pauling's equation is independent of the oxidation number the element exhibits. This conclusion is in direct contradiction to that of HAÏSSINSKY.[6] He had calculated the electronegativity from Pauling's equation. However, as PRITCHARD and SKINNER have indicated HAÏSSINSKY assumed the bond energy of M–M bond to be invariant no matter what the oxidation state of the element was. This assumption, they claimed, may be "a very questionable one". It might be wise to reiterate that the results obtained with either equation (6) or (7) does not depend on any assumptions concerning the B(M–M) for the different valence states. Our conclusion, therefore, agrees with that of PRITCHARD and SKINNER.

There are presented for the first time electronegativity values calculated from thermochemical data for most of the lanthanides and four of the actinides. In the case of the lanthanide series, only one value could be calculated for each element. As was to be expected, the values of this family of elements agreed among themselves very well. Except for thorium, the elements of the actinide series for which x_M was calculated agreed very well among themselves and, indeed, very well with the lanthanide series.

It should be mentioned that other schemes of reactions can be devised in which the electronegativity of an element could be directly related to a heat of reaction and other thermochemical information and in which the nature of the M–M bond and its bond energy need not be known. The method presented in this paper is believed to be one of the simplest and most direct since it involves only heats of formation of two halides of the element and, in some instances, the heat of vaporization of bromine and heat of sublimation of iodine.

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CHEMICAL EFFECTS IN FISSION RECOIL—IV

THE EFFICIENCY OF RECOILING ATOMS IN THE DECOMPOSITION OF POTASSIUM NITRATE

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Abstract—Previous experiments on the decomposition of potassium nitrate by fission fragments recoiling from uranium foils have been repeated using thin films of uranium oxide enriched in ^{235}U. Fragments recoiling from very thin layers are found to be about 2·7 times more efficient in causing decomposition than fragments recoiling from an effectively infinitely thick source. Measurements on the decomposition caused by fragments emerging from aluminium absorbers show that at the ends of the tracks the yield per 100 eV of ionizing energy is more than the average for the whole track, but that the yield per 100 eV of total energy does not appear to change appreciably. The average G factor for the decomposition has been redetermined as 6·0 nitrite ions per 100 eV of recoil energy absorbed.

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THE decomposition caused by fission fragments recoiling through potassium nitrate has previously been studied[1] by the irradiation of a flat disk of the nitrate held between uranium metal foils. Measurements were made on the amount of nitrite formed and on the radioactivity of fission fragments stopping in the potassium nitrate phase. As the adjoining surfaces were planar it was possible to estimate the fraction of the recoil energy expended in the nitrate phase, and hence to obtain the efficiency of the recoiling fragments as a decomposing radiation. Two major difficulties were encountered. In the first place decomposition by pile background radiation was comparable to the decomposition caused by the fission fragments. This background decomposition was also found to be variable and appeared to depend in a sensitive manner on the quality of the potassium nitrate phase. Secondly, as the uranium metal was considerably thicker than the recoil range, the more penetrating radiations arising from fission in the bulk of the uranium also had a significant effect on the total decomposition. The former effect can be reduced to a relatively lower level by the use of enriched fissile material, and the replacement of thick metal by a film of oxide which is thin compared to the recoil range minimizes the second effect.

The calculation of the fraction of recoil energy retained by fission fragments emerging from an effectively infinitely thick layer was previously made[2] on the basis of the approximations that all fission fragments have the same range, and that the energy E is related to the residual range R by an expression of the form

$$E = aR^2 \qquad (1)$$

where a is a constant for all fragments.

It is known that these are gross approximations and it was decided to measure the effective energy retained by fragments recoiling from layers ranging from those

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[1] D. HALL and G. N. WALTON, *J. Inorg. Nucl. Chem.* **6**, 288 (1958).

[2] G. N. WALTON and I. F. CROALL, *J. Inorg. Nucl. Chem.* **1**, 149 (1955).

which are effectively infinitely thick to very thin layers. The effective energy was measured by the amount of decomposition in the adjacent layer of potassium nitrate.

According to the theory of the slowing down of fission fragments in matter[3] energy loss occurs mainly by two processes. Most of the energy is lost by electronic interaction between the charged particle and the cloud of electrons through which it moves, producing ionization in the medium. At low velocities the particle has insufficient energy to cause ionization and an appreciable fraction of the energy is lost by nuclear collision processes without causing ionization. As shown in a previous paper[1] γ-radiation and fission fragments do not have the same efficiency in causing decomposition for equal energy deposition, and it was considered possible that the efficiency along a fission fragment track might also vary. It was decided to investigate this by measuring the decomposition produced by fragments after traversing different thicknesses of aluminium. In the absence of aluminium the mean decomposition could be observed for the whole track, whereas after traversing aluminium of thickness comparable to the range of the fragments, decomposition would be observed only at the ends of the tracks.

EXPERIMENTAL

The technique used was essentially that described previously.[1] The potassium nitrate was pressed into thin smooth disks under a standard pressure (1200 lb/in^2) and with a fixed duration of 1 min. The disks were all prepared from the same homogeneous sample of A.R. potassium nitrate. The uranium oxide (enriched sixtyfold in ^{235}U) films were prepared on platinum backings, by measuring out onto the platinum the requisite volume of a solution of enriched uranyl nitrate, so as to cover a defined area, drying off and finally igniting to the oxide. A spreading agent (tetraethylene glycol) was used to obtain uniform films. The potassium nitrate disk was sandwiched between the uranium films and this assembly was irradiated in BEPO in a silica capsule. Silica was used as the containing material rather than glass in order to reduce thermal neutron absorption and hence to increase the ratio of thermal neutron to background radiation. The pile irradiation position was chosen so as to have a high thermal to fast neutron flux ratio, although this entailed the use of a rather low flux (10^{10} neutrons cm^{-2} sec^{-1}). The hole chosen was some distance from the majority of other irradiation sites and was not closely exposed to local fluctuations in radiation quality. For each irradiation a cobalt monitor was used. This consisted of a weighed piece of thin cobalt wire which was subsequently counted for ^{60}Co activity and this activity provided a reasonably accurate measure of the total radiation dose received by the sample. Irradiation times were normally in the range 1–12 hr.

After irradiation, the nitrate was dissolved and analyses for nitrite, ^{89}Sr and ^{140}Ba, were carried out as described previously.

To obtain an aluminium absorption curve for fission recoils, thin foils of aluminium were inserted between the uranium oxide film and the potassium nitrate. In view of the irregular thickness of the large sheets of aluminium from which the absorbers were made, each was weighed separately.

It has been shown[1] that the yield of nitrite appears to be linearly dependent on the number of fission recoils up to about 5 per cent. In this present work irradiation times were chosen such that this level was not exceeded.

RESULTS

A check on the consistency of results was made by irradiating several samples of potassium nitrate simultaneously in contact with thin uranium films of identical thickness. Measurements were made on the amount of decomposition, on the activity generated in a cobalt monitor and on the amount of ^{140}Ba appearing in the nitrate phase. A similar experiment was performed using samples without uranium so as to find the decomposition due to pile background radiation. The results are listed in Table 1. From the relative values found for the cobalt monitor (columns 3

[3] N. BOHR, *Det. Kgl. Dansk. Videnskab. Selskab. Mat. Fys. Medd.* **18**, 8 (1948).

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and 7) and from the weight of potassium nitrate exposed (columns 1 and 5), the decomposition due to pile background could be calculated for the recoil experiments. This was subtracted from the decomposition observed (column 6) to find the decomposition which could be attributed to fission recoils (column 8). As both the source and the target were thin the decomposition due to penetrating radiations emitted from the uranium other than fission recoils, i.e. α-, β- and γ-radiation, was estimated to be negligible. It was also assumed that the introduction of the uranium did not alter

TABLE 1.—FISSION RECOIL AND BACKGROUND EFFECTS

BACKGROUND EXPERIMENTS

1 KNO_3 irradiated (mole × 10^{-6})	2 NO_3^- formed (mole × 10^{-6})	3 Activity of cobalt monitor (counts/min per mg)	4 NO_3^- formed per μmole of KNO_3 per counts/min of cobalt (mole × 10^{-12})
634	0·268	39050	0·108
416	0·206	38570	0·128
688	0·323	37870	0·124
676	0·316	37560	0·124

RECOIL EXPERIMENTS

5 KNO_3 irradiated (mole × 10^{-6})	6 NO_3^- formed (mole × 10^{-6})	7 Activity of cobalt monitor (counts/min per mg)	8 NO_3^- corrected for background (mole × 10^{-6})	9 Activity of ^{140}Ba (counts/min)	10 NO_3^- formed per counts/min of ^{140}Ba (mole × 10^{-11})
571	0·740	6040	0·698	10520	6·63
599	0·777	6330	0·731	10780	6·78
650	0·759	5820	0·713	10810	6·60

the neutron flux in the vicinity of the sample appreciably. As previously observed[1] the decomposition due to pile radiation alone shows considerable variations and it would appear that a more elaborate procedure would be required to produce disks that are reproducible in this respect. The background correction was not large and throughout these experiments variations in the yield of nitrite relative to fission product activity appeared to be much smaller than variations in the pile background effect.

In Table 2 results are listed for the experiments using uranium sources of different thicknesses.

Irradiation times were chosen such that in each case approximately the same amount of decomposition occurred. Analyses were made for ^{89}Sr and ^{140}Ba in the nitrate phase and figures for the activity at the end of the irradiation are shown in the table. No appreciable decay occurred during the irradiation. The approximate numbers of light and heavy fragments recoiling into the nitrate phase were calculated

TABLE 2.—VARIATION OF DECOMPOSITION WITH SOURCE THICKNESS

Thickness of U_3O_8, (mg/cm²)	Total decomposition NO_3^-, (mole × 10^{-6})	Decomposition corrected for bkgd. NO_3^-, (mole × 10^{-6})	Activity of ^{89}Sr (dis/min)	Activity of ^{140}Ba (dis/min)
0·113	0·1996	0·1817	—	29,380
0·354	0·2404	0·2290	8,320	43,280
1·72	0·2044	0·2027	9,760	49,400
5·89	0·2056	0·2046	14,930	65,440

assuming that the fraction of strontium fragments undergoing self-absorption in the source represented the average self-absorption for all the light fragments, and that barium represented the average for the heavy fragments. The total numbers of light and heavy fragments were thus calculated from the fission yields of the two products measured (4·8 and 6·44 per cent respectively). The ratio of light to heavy fragments is plotted in Fig. 1 as a function of uranium thickness, and the yield of nitrite per fragment is similarly plotted in Fig. 2.

The decomposing efficiency of fission fragments over different parts of the range was investigated by placing thin aluminium absorbers between the uranium and the target surfaces. All samples were irradiated for the same time using uranium sources of the same thickness, i.e. U_3O_8 0·53 mg/cm². Results are recorded in Table 3. For those samples in which the aluminium thickness was less than 2 mg/cm² only one uranium film was used, while for the thicker absorbers the potassium nitrate was sandwiched between two films, the thicknesses of which are quoted separately in the table. This assisted in increasing the decomposition due to fission recoils relative to the decomposition due to pile background. Table 3 shows the decomposition before

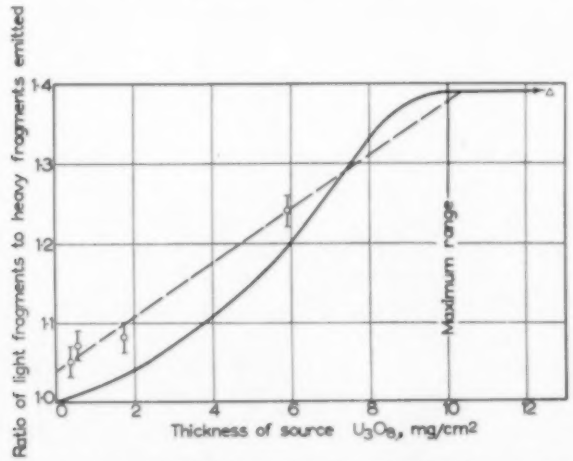

FIG. 1.—Ratio of light and heavy fragments emitted from thick sources.
T observed points for U_3O_8
△ observed point for thick uranium metal
— theoretical ratio for two groups of fragments with defined ranges

TABLE 3.—VARIATION OF DECOMPOSITION WITH ABSORBER THICKNESS

Absorber thickness aluminium (mg/cm²)	Total decomposition NO_3^- (mole × 10^{-6})	Decomposition corrected for bkgd. NO_3^- (mole × 10^{-6})	Activity of ^{89}Sr (dis/min)	Activity of ^{140}Ba (dis/min)
0	0·715	0·663	25,140	123,700
0·28	0·494	0·459	22,710	107,100
0·64	0·344	0·308	19,810	93,290
1·03	0·202	0·171	17,740	64,540
1·32	0·156	0·120	14,960	59,510
1·65	0·107	0·085	12,580	46,100
2·08 2·12	0·134	0·093	24,040	60,830
2·32 2·29	0·098	0·061	21,390	45,990
2·61 2·59	0·070	0·033	(15,200)*	28,840

* Extrapolated value

and after correcting for the background effect, together with the activity of the ^{89}Sr and ^{140}Ba found in the nitrate phase. Fig. 3 shows a plot of the total decomposition relative to the amount of strontium and barium after traversing different thicknesses of aluminium.

DISCUSSION

Effect of uranium source thickness

For thick sources the number of light fragments emerging during fission would be expected to be greater than the number of heavy fragments because of the different ranges. For very thin sources the ratio would be expected to be unity and the ratio

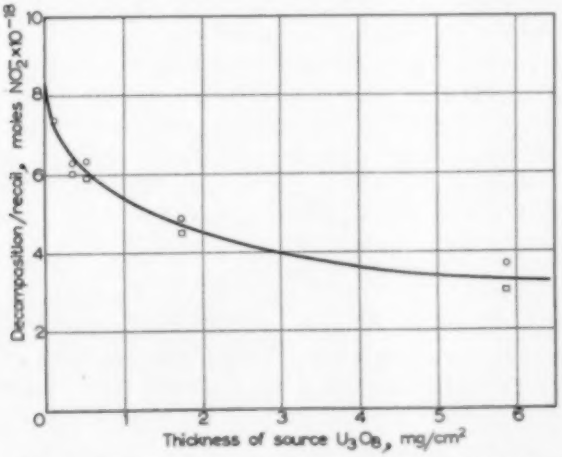

FIG. 2.—Decomposition by fragments recoiling from thick sources.
○ Calculated from ^{140}Ba
□ Calculated from ^{89}Sr

should increase with increasing thickness of source until the thickness reaches the maximum range, after which the ratio should remain constant at a value corresponding to the ratio of the ranges (see Appendix). These effects are seen in Fig. 1. This shows the ratio of the strontium to barium atoms emitted from the uranium divided by the ratio of their fission yields. The plot extrapolates to about 1·03 at zero uranium thickness. The uncertainties shown for the points represent the standard deviations of the analytical results. The ratio also involves correction factors for β-ray scattering and absorption in absolute counting, which may have uncertainties up to about 5 per cent. For thick uranium metal foil the ratio for the emission of strontium to barium was previously observed to be 1·39.[1] The line through this value in Fig. 1 cuts the thin oxide line at a thickness of about 10·0 mg/cm² which is the value estimated by SEGRÈ and WIEGAND[4] for the maximum extrapolated range of fission fragments in uranium oxide. The ratio of the ranges of strontium and barium in aluminium has been measured to be 1·33,[5] but the ratio has not been measured previously in uranium metal or oxide. In gold the ranges of the median light and heavy fragments has been reported to be 12·5 mg/cm² and 9 mg/cm² respectively.[6] Here the ratio is 1·39 and if particles are assumed to be grouped into two ranges the ratio of the particles emerging should follow the continuous line shown in Fig. 1. Dispersion in ranges would be expected to smooth the curve so as to approach a more linear plot.

Since the energy of the heavier particle is more highly absorbed in a thick source than that of the light particle, the apparent nitrite yield per fragment is greater if calculated from the ^{140}Ba activity than from the ^{89}Sr activity. The results of these calculations are plotted in Fig. 2 where the mean curve is drawn. This extrapolates to a value of about $8{\cdot}3 \times 10^{-18}$ mole of nitrite per recoil at zero thickness, and about $3{\cdot}1 \times 10^{-18}$ mole at infinite thickness. The ratio between these is 2·7, and it is apparent that the former deduction,[2] that the zero thickness value should be three times the infinite thickness value, is only approximately correct.

It is also seen that the yield formerly obtained[1] for thick uranium metal, i.e. $4{\cdot}8 \times 10^{-18}$ mole per recoil is too high. In the former measurements made with natural uranium a large correction had to be introduced for the pile background effect, and also for the effect of penetrating radiations emitted from the uranium. It is possible that these corrections were not sufficient, but the apparent difference between the decomposition caused by fission fragments arising from thick uranium metal and those from thin uranium oxide requires further investigation. From the value of $8{\cdot}3 \times 10^{-18}$ mole of nitrite per recoil, and assuming 83·5 MeV expended per recoil, the average G factor for the formation of nitrite in potassium nitrate is 6·0 molecules per 100 eV absorbed.

Effect of aluminium absorbers

To evaluate the aluminium absorption curves shown in Fig. 3 it is necessary to know the energy lost by the recoil in passing through the aluminium. Two previous measurements have been made of the rate of energy loss by fission fragments as they pass through matter. The first study was made by LASSEN[7] in which he measured

[4] E. SEGRÈ and C. WIEGAND, *Phys. Rev.* **70**, 808 (1946).
[5] L. LEROUX and G. N. WALTON, To be published.
[6] C. B. FULMER, U.S.A.E.C. Report ORNL-2320 (1957); *Phys. Rev.* **108**, 1113 (1957).
[7] N. O. LASSEN, *Det. Klg. Dansk. Videnskab. Selskab. Mat. Fys. Medd.* **25**, 11 (1949).

the ionization produced in gases as a function of the distance travelled through the gas for the light and heavy fragments, resolved as two groups. Measurements were also made on the ionization produced in a gas by fission fragments emerging from different thicknesses of mica. The curves obtained approximate closely to a parabolic relationship of the form shown in equation (1).

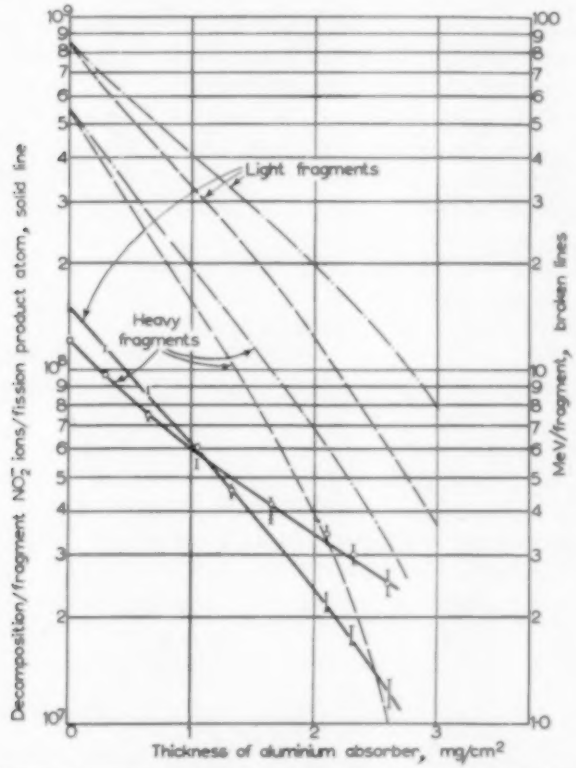

FIG. 3.—Energy of fragments emitted through absorbers and the decomposition produced.
Decomposition from ^{140}Ba measurements
Decomposition from ^{89}Sr measurements
---- Energy from ionization measurements
—·—·— Energy from scintillation measurements

The second study was made very recently by FULMER[6] in which the size of the scintillations produced by fission fragments stopping in a caesium iodide detector was measured as a function of the thickness of various absorbers through which the fragments passed. The pulse height versus energy calibration was obtained by comparison with observations on the velocity of fragments emerging from nickel and aluminium as measured by SCHMITT and LEACHMAN.[8,9] The resulting curves, however, for the energy left in a fragment after traversing much of its range differ by over a factor of two from those of LASSEN, (Fig. 27 in ref. 6, and Fig. 24 in ref. 7). FULMER's curves do not approximate to any simple power relationship and in using

[8] H. W. SCHMITT and R. B. LEACHMAN, *Phys. Rev.* **102**, 183 (1956).
[9] R. B. LEACHMAN and H. W. SCHMITT, *Phys. Rev.* **96**, 1366 (1954).

them to evaluate the absorption curves of Fig. 3 it has been necessary to integrate numerically.

The integration has been carried out by considering the fragments emerging in solid angle increments of 5° from the normal to the surface of the absorbers. Knowing the total range of strontium and barium in the aluminium, and in the uranium oxide source, the residual range of a fragment emerging at any angle from the normal could be calculated and also the number emerging in the corresponding solid angle increment. The energy of these fragments was then read off from FULMER's or LASSEN's curves. The total energy of the emerging fragments was then summed over all the angles for any one absorber. Dividing by the number of emerging fragments gave the average energy per fragment for the different absorber thicknesses. The uranium oxide thickness was considered as equivalent to one half the corresponding thickness of aluminium and involved only a small correction.

The following parameters were used:

Range of strontium in aluminium	4·38 mg/cm²
Range of barium in aluminium	3·29 mg/cm²
Thickness of uranium oxide source	0·53 mg/cm²
equivalent to	0·097 mg/cm² of aluminium absorber.

(From SEGRÈ and WIEGAND[4] 10 mg/cm² of U_3O_8 is equivalent in stopping power to 3·7 mg/cm² of aluminium.)

Energy of light fragments (before absorption)[10]	100·2 MeV
Energy of heavy fragments (before absorption)[10]	66·9 MeV

For LASSEN's energy curve the numerical method was checked by an algebraical integration of equation (1) which gave substantially the same result (see Appendix).

The results of the numerical integration are plotted in Fig. 3 to show the average energy of emerging fragments as a function of absorber thickness. In general the energy curves are steeper than the decomposition curves especially for the heavy fragments. The effective G value was obtained from equation (2).

$$G = 100M\left(\frac{D_1E_1}{\lambda_1\alpha_1} + \frac{D_2E_2}{\lambda_2\alpha_2}\right)^{-1} \tag{2}$$

where M is the number of molecules of nitrite formed, D_1 and D_2 are the disintegration rates of the strontium and barium observed at the end of the irradiation, E_1 and E_2 are the average energy in electron volts per fragment for the light and heavy fragments emerging from the absorbers, λ_1 and λ_2 are the decay constants of strontium and barium, and α_1 and α_2 are the fission yields. Values of G for the two sets of calculations are shown in Fig. 4. The value of G shown here for zero absorption is lower than that calculated from Fig. 2 where values of G were obtained from thinner sources. Of the two sets of data, LASSEN's probably have less uncertainties in the energy calibration than FULMER's. Fig. 4 clearly shows that the amount of decomposition in potassium nitrate relative to the ionizing energy of the fission fragments increases towards the end of the fission fragment track. However, as previously reviewed[10] it is well established that fission fragments dissipate a considerable fraction (the ionization defect), of their energy by nuclear collisions without causing ionization, and theory[3] suggests that this fraction increases towards the end of the

[10] G. N. WALTON, *Prog. Nucl. Phys.* **6**, 192 (1957).

fission fragment range. If it is assumed that the scintillation measurements detect this energy in addition to the ionization energy, then it would appear that the decomposition along the length of the track closely follows the total energy deposition. Nevertheless the discrepancy between the curves is too great to be accounted for by the ionization defect alone, and the range–energy relationship for fission fragments at the end of their tracks requires further study.

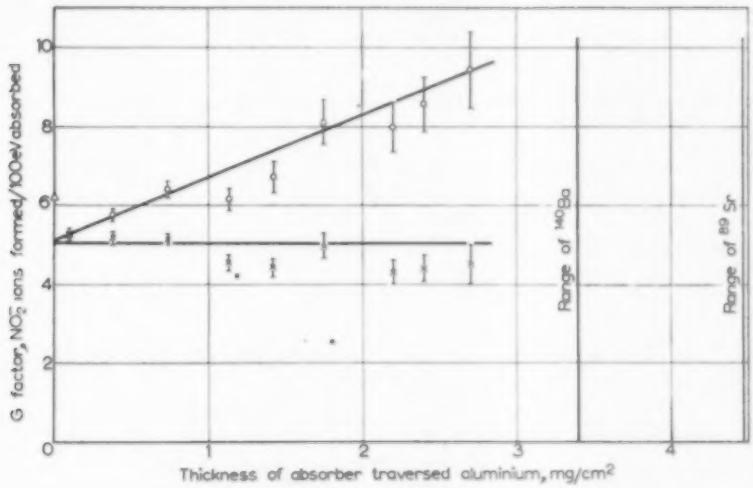

FIG. 4.—Average G factor over different parts of the range.
From ionization measurements
From scintillation measurements
△ From thin source measurements.

Acknowledgements—The authors wish to thank Mr. E. B. FURBY for preparing the uranium sources and Miss M. L. SIZELAND for assisting with the experiments.

APPENDIX

Energy of fission fragments emerging from absorbers covering a thick source

1. *Number emitted.* Consider fragments travelling in straight tracks of range R_0.

The number δN emitted from a thin layer of thickness δx in a plane source of area A in a direction θ from the normal to the source in a solid angle increment $\delta\theta$ is given by

$$\delta N = \tfrac{1}{2} A N_0 \sin\theta \, \delta\theta \, \delta x$$

where N_0 = number generated per cm³ in the source.

If d is the thickness of the absorber fragments will not be emitted at angles greater than $\cos^{-1}\dfrac{x+d}{R_0}$ to the normal.

The total number N_t emitted from a source of thickness s through an absorber of thickness d is therefore given by

$$N_t = \int_{x=0}^{x=s} \int_{\theta=0}^{\theta=\cos^{-1}\frac{x+d}{R_0}} \tfrac{1}{2} A N_0 \sin\theta \, d\theta \, dx$$

Integrating,

$$N_t = \tfrac{1}{2}AN_0 s\left(1 - \frac{s+2d}{2R_0}\right), \; d \text{ and } s \not> R_0$$

The ratio of two products of different ranges R_1 and R_2 emitted from a thick source with no absorbers is given by

$$\frac{N_1}{N_2} = \frac{s(2R_1 - s)}{s(2R_2 - s)} \cdot \frac{R_2}{R_1}$$

N_1 and N_2 reach maxima when $s = R_1$ and $s = R_2$ and therefore the ratio reaches a steady value when

$$\frac{N_1}{N_2} = \frac{R_1}{R_2}$$

2. *Energy emitted.* If the energy of a single fragment is related to the residual range R by

$$E = f(R)$$

then from the previous section the total energy E_t carried by all the fragments emitted from the absorber is given by

$$E_t = \int_{x=0}^{x=s} \int_{\theta=0}^{\theta=\cos^{-1}\frac{x+d}{R_0}} \frac{AN_0}{2} f\left(R_0 - \frac{x+d}{\cos\theta}\right) \sin\theta \, d\theta \, dx$$

If $E = aR^2$ this may be integrated to give

$$E_t = a\frac{AN_0}{2}\left[R_0^2 s - \frac{1}{3}(s+d)^3 - d^3 + R_0 s(s+2d)\left\{\ln\left(\frac{s+d}{R_0}\right) - \frac{1}{2}\right\} + R_0 d^2 \ln\left(\frac{s+d}{d}\right)\right].$$

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THE HOT ATOM CHEMISTRY OF ORGANIC PHOSPHORUS COMPOUNDS—I

THE PRODUCTS OF NEUTRON IRRADIATION OF TRIBUTYL PHOSPHATE

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Abstract—A study has been made of the chemical effects of neutron capture in tributyl phosphate. A procedure is given for fractionation of the inorganic ^{32}P, and preliminary fractionation of the ^{32}P in organic combination. Retention of ^{32}P in organic combination has been studied as a function of neutron dose rate. Inorganic ^{32}P is present predominantly as orthophosphate in the final products, a small percentage of the total activity also being present as orthophosphite.

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THE great majority of systematic studies of the formation of organic compounds by hot atoms has been done with halogen atoms activated by neutron capture. The advantages of organic halides for such work are their relatively well known chemistry and the existence of an extensive background of photochemical studies of these compounds. The latter feature allows comparison of activation or radical mechanisms in hot atom studies with the better known mechanisms prevailing during photo-irradiation.

Much less has been done to study the hot atom chemistry of organic compounds of polyvalent atoms. In earlier work Szilard–Chalmers reactions were studied for organic compounds of arsenic, antimony, bismuth, tellurium, phosphorus, tin and lead.[1,2] In these studies, however, interest was mainly centred on obtaining isotope preparations of high specific activity, and although the division of activity between organic phase and various aqueous extractants was examined, the mechanism of retention in the organic phase was not studied. More recently studies have been made of the products of neutron irradiation of triphenyl arsine[3] and triphenyl stibine,[4] in which the various products of reaction of the activated arsenic and antimony atoms have been carefully examined. Apart from the activity remaining in the irradiated compounds and the activity which comes to be present in inorganic forms, several active monophenyl and diphenyl arsenic and antimony compounds have been identified.

It would seem that such systems offer interesting possibilities for studying the possible role both of radical type mechanisms[5] and "billiard-ball" collisions[6] in the retention of activity in organic combination. For example, neutron irradiations of arsenic trichloride in benzene have shown formation of monophenyl and diphenyl

[1] G. T. SEABORG, G. FRIEDLANDER and J. W. KENNEDY, *J. Amer. Chem. Soc.* **62**, 1309 (1940); W. MAURER and W. RAMM, *Z. Phys.* **119**, 609 (1942); H. SPANO and W. KAHN, *J. Amer. Chem. Soc.* **74**, 568 (1952).
[2] L. MELANDER, *Acta Chem. Scand.* **2**, 290 (1948); R. R. WILLIAMS, *J. Phys. Coll. Chem.* **52**, 603 (1948).
[3] N. SUTIN and A. G. MADDOCK, *Trans. Faraday Soc.* **49**, 1150 (1953).
[4] R. M. S. HALL and N. SUTIN, *J. Inorg. Nucl. Chem.* **2**, 184 (1956).
[5] J. E. WILLARD, *Ann. Rev. Nucl. Sci.* **3**, 193 (1953).
[6] W. F. LIBBY, *J. Amer. Chem. Soc.* **69**, 2523 (1947).

compounds of active arsenic, in conditions which preclude intervention of a billiard-ball type mechanism.[7] The existence after irradiation of compounds of the activated atom in which one, two or three bonds with organic residues are present should permit of examination of factors governing the relative probabilities of rupture of one, two or three bonds during the primary act of escape, and also the examination of the influence of such factors as radical concentration, phase conditions and presence of competing inorganic species on the relative probabilities of the formation by a naked hot atom of one, two or three bonds with organic residues.

In the present work a procedure has been developed and applied for determining some of the possible organic and inorganic products of neutron irradiation of tributyl phosphate (TBP), which has been selected as a further system for study of the mechanisms of formation of organic compounds by hot polyvalent atoms. In subsequent work the mechanisms of formation of these products will be examined.

The only previous work on Szilard–Chalmers reactions of phosphorus esters is a study of the neutron irradiation of triphenyl phosphate in benzene by ERBACHER and PHILIPP,[8] who found that 40 per cent of the induced ^{32}P activity after bombardment could be extracted with pure water, but did not identify the compounds present in the aqueous or organic phases.

EXPERIMENTAL METHODS

TBP was freed from monobutyl phosphate (MBP), dibutyl phosphate (DBP), and butyl alcohol by the method of MCKAY,[9] and, if used for pile irradiation, distilled under vacuum at 130–160°C. and sealed in quartz ampoules for irradiation. Pile irradiation was done at a neutron flux of approximately 10^9 neutrons cm^{-2} sec^{-1} in the thermal column of the Jener heavy water experimental reactor at Kjeller and ca. $9 \cdot 10^{10}$ and $9 \cdot 10^{11}$ neutrons cm^{-2} sec^{-1} in the thermal column of the experimental reactor "EWA", of the Institute of Nuclear Research at Swierk. Irradiation at a lower level was done with 800 ml portions of TBP, located at an average distance of 8 cm from a 500 mg Ra/Be source in paraffin wax.

To check for phosphine activity the quartz ampoule after irradiation was broken in a closed vessel in an atmosphere of nitrogen and inactive phosphine, followed by bubbling a stream of nitrogen and phosphine, generated by the action of hydrochloric acid on aluminium phosphide, through the sample. The phosphine stream passed via a glass wool droplet trap to three scrubbers each containing 50 ml of 0·02 M $AgNO_3$ in 0·7 M NH_4OH. The brownish black precipitate from each scrubber was dissolved in approximately 7·5 M HNO_3 for activity estimation with a glass-walled immersion counter.

To separate all other activities from TBP, it was proposed to extract with sodium hydroxide solution, which is known to remove monobutyl phosphate (MBP) and dibutyl phosphate (DBP) and which will extract all inorganic forms. To separate MBP and DBP from the alkaline extract, an extraction process with organic solvents after acidification seemed attractive both for speed and simplicity. Wide differences have been reported for partition coefficients of MBP and DBP at high concentrations from aqueous solutions into various solvents.[10] Thus it seemed advisable to check the proposed extractions carefully, both in order to measure the partition coefficients for MBP and DBP present in small concentrations as carriers and so as to allow setting-up of a separation procedure of adequate selectivity, and also to estimate the amounts of inorganic phosphorus compounds which might also be extracted with the organic solvents. For this purpose individual compounds whose behaviour was to be studied in the extraction process were prepared labelled with ^{32}P.

Table 1 shows the partition coefficients of MBP and DBP between organic and aqueous phase

[7] E. SIEKIERSKA, A. SOKOLOWSKA and I. G. CAMPBELL, *J. Inorg. Nucl. Chem.* To be published.
[8] O. ERBACHER and K. PHILIPP, *Z. Phys. Chem.* A **179**, 263 (1937).
[9] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[10] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).

TABLE 1.—PARTITION COEFFICIENTS K = org./aq., FOR MBP AND DBP IN VARIOUS SOLVENTS

(1) Organic solvent	(2) Composition of aqueous phase	(3) pH of aqueous phase	(4) K_{MBP}	(5) K_{DBP}
C_6H_6	MBP* 5 mg/ml DBP 5 mg/ml	1·77	≤0·0015	
C_6H_6	MBP* 3 mg/ml DBP 3 mg/ml H_3PO_4 3 mg/ml	1·77	≤0·0015	
C_6H_6	MBP* 3 mg/ml DBP 3 mg/ml H_3PO_4 3 mg/ml	0·87	≤0·0023	
C_6H_6	MBP* 3 mg/ml DBP 3 mg/ml H_3PO_4 3 mg/ml	0·16	0·035	
C_6H_6	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	1·60		4·50
C_6H_6	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	0·87		7·77
C_6H_6	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	0·10		13·0
n-$C_5H_{11}OH$	MBP* 5 mg/ml DBP 5 mg/ml	1·97	0·99	
n-$C_5H_{11}OH$	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	1·70		48·6
CCl_4	MBP* 5 mg/ml DBP 5 mg/ml	1·80	≤0·0013	
CCl_4	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	1·62		2·44
TBP	MBP* 5 mg/ml DBP 5 mg/ml	2·10	1·14	
TBP	MBP 5 mg/ml DBP* 5 mg/ml H_3PO_4 5 mg/ml	1·65		21·5

* Denotes component labelled with ^{32}P.

for four different solvents, using ^{32}P labelled mono and di-esters. Equal phase volumes were used in these experiments, and partition coefficients determined by activity measurements with an immersion counter, with appropriate density corrections, after separating the phases. It can be seen that benzene is a good solvent for separating DBP from an aqueous solution of DBP + MBP + carrier phosphate, at pH 0·5–1·0, and this procedure has been used in the subsequent experiments.

It would also seem that *n*-amyl alcohol could be used to extract MBP from the aqueous phase after removal of DBP. Since partition coefficients of the various phosphorus acids from aqueous solutions into amyl alcohol are not given in the literature, the extraction of small amounts of other phosphorus acids was also studied. Figs. 1 and 2 show the relationship between pH and partition coefficients for ^{32}P-labelled MBP, H_3PO_4, H_3PO_3, $H_4P_2O_6$, and $H_4P_2O_7$. The ratio $K_{MBP}/K_{H_3PO_4}$

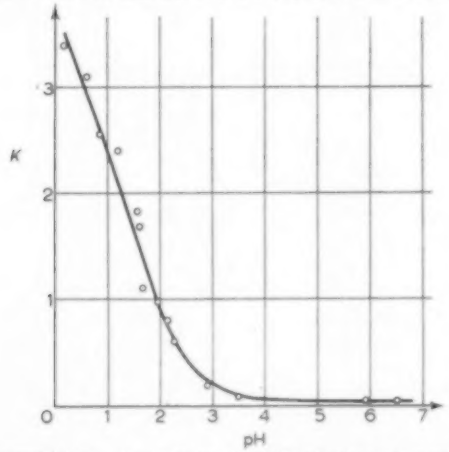

FIG. 1.—Partition coefficient, -K = org./aq., for MBP in the system *n*-amyl alcohol–water as a function of pH. Composition of aqueous phase: MBP* 1·5 mg/ml DBP 1·5 mg/ml H_3PO_4 1·5 mg/ml.

rises to a flattish maximum in the region pH 0·5–1·0. Since orthophosphate was expected to be the most prominent inorganic compound of phosphorus produced by neutron irradiation of TBP, a pH 0·5–1·0 was used in the amyl alcohol extraction to minimize the proportion of inorganic ^{32}P extracted into the alcohol.

The following method can thus be proposed for separating DBP, MBP and ortho-phosphoric acid from the irradiated TBP. To the irradiated TBP are added carrier MBP, DBP and H_3PO_4, and the solution is then extracted twice with an equal volume of ca. 0·3 M NaOH. The pH of the pooled aqueous extracts is then brought to 0·5–1·0 and the solution is extracted twice with an equal volume of benzene. The aqueous phase is then extracted twice with an equal volume of *n*-amyl alcohol.

In order to check the overall separation scheme, ^{32}P-labelled MBP, or DBP or H_3PO_4 were added to inactive TBP, the other two appropriate unlabelled carriers were added, and the mixture subjected to the above fractionation scheme. From measured values of pH and the data of Table 1 and Figs. 1 and 2 the proportion of activity to be expected in each fraction was calculated and compared with the measured values. The results are shown in Table 2.

It can be seen that DBP is well separated into the benzene fraction. The separation of H_3PO_4 from MBP is less satisfactory, but is considered adequate for the present work. The above scheme has therefore been applied. It must, of course, be remembered that compounds of phosphorus other than DBP and MBP formed with fragments of butyl chains might come to be present in the benzene or amyl alcohol fractions.

The coefficients of partition of H_3PO_4, H_3PO_3, $H_4P_2O_6$ and $H_4P_2O_7$ from water into benzene, as measured by us with ^{32}P-labelled compounds, are as is to be expected, very low ($\leq$0·001, $\leq$0·003, $\leq$0·002 and $\leq$0·001).

In order to ascertain the nature of the aqueous activity after benzene and amyl alcohol extractions, it was decided to test procedures for:—

(a) precipitation of orthophosphate as phospho-molybdate

(b) reduction of hypophosphite, and orthophosphite to phosphine, with nascent hydrogen.
(c) precipitation of pyrophosphate and hypophosphate together as barium salts.
Hexametaphosphate was precipitated as barium salt at low pH.

In view of the extractability into amyl alcohol of a certain amount of inorganic ^{32}P, as shown in

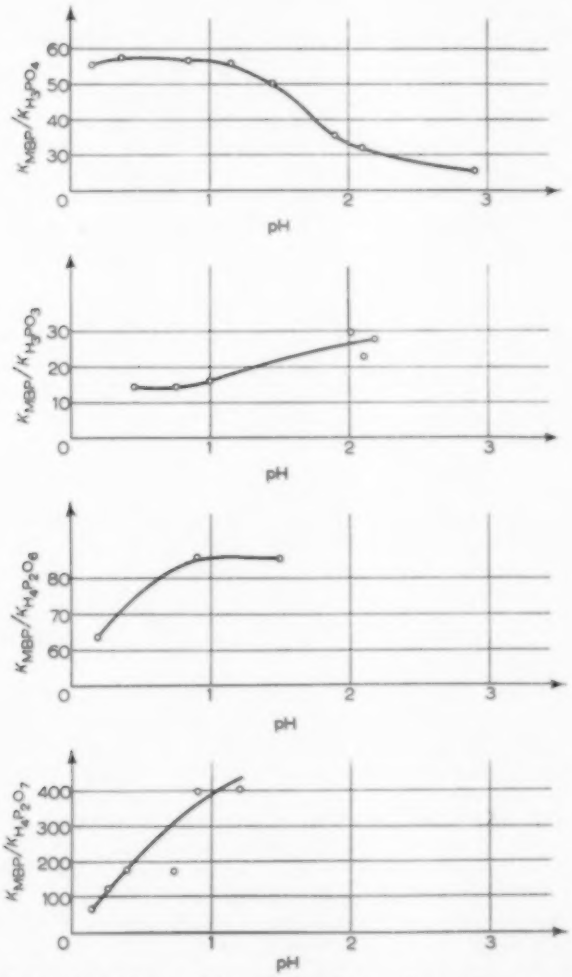

FIG. 2.—Ratio of partition coefficient K_{MBP} to $K_{H_3PO_4}$, $K_{H_3PO_3}$, $K_{H_4P_2O_6}$ and $K_{H_4P_2O_7}$ in the system *n*-amyl alcohol–water as a function of pH. Composition of aqueous phases:
MBP* 1·5 mg/ml H_3PO_4* 1·5 mg/ml H_3PO_3* 2 mg/ml
$H_4P_2O_6$* 2 mg/ml $H_4P_2O_7$* 2 mg/ml

Figs. 1 and 2, it was considered that it might sometimes be necessary to precipitate inorganic phosphorus compounds from the aqueous extract before a benzene or an amyl alcohol extraction. Therefore it was considered necessary to examine the possibility of co-precipitation of MBP, and the effects of the presence of small amounts of added MBP carrier on the completeness of precipitation of orthophosphate by ammonium molybdate. The experiments of Table 3 were performed.

It can be seen from Table 3 that the presence of carrier amounts of MBP does not prevent the precipitation of orthophosphate from being sensibly complete. Precipitates formed at room temperature and also after warming show the presence of a few per cent of ^{32}P coming from MBP, but the

separation is sufficient for the purposes of the present experiments, and accordingly the method of experiment 12 has been used subsequently to precipitate orthophosphate in the presence of MBP.

The presence of DBP does not influence molybdate precipitations, since 0·1 ml of DBP brought to 40–50°C and shaken for 10 min in 100 ml of a solution containing 50 ml of ammonium molybdate solution[11] gave no trace of precipitate or appreciable colour in the solution after 48 hr standing.

The possibility of bringing down ^{32}P from pyrophosphate together with orthophosphate during precipitation of the latter as phosphomolybdate was examined using ^{32}P-pyrophosphate. JONES[12]

TABLE 2.—DISTRIBUTION OF MBP*, DBP* AND H_3PO_4* IN FRACTIONS OF EXTRACTION SCHEME

Experiment No	Compound labelled	Total activity in fraction (%)						
		TBP after NaOH extraction	Benzene extracts		*n*-Amylalcohol extracts		H_2O after extraction	
			Theor.	Obs.	Theor.	Obs.	Theor.	Obs.
1	MBP*	0·00		0·09	86·6	85·7	13·4	14·2
2	MBP*	0·00		0·21	91·8	89·6	8·2	10·1
3	DBP*	1·1	99·8	97·3			0·2	1·50
4	DBP*	1·3	99·8	97·7			0·2	1·00
5	H_3PO_4*	0·00		0·00	9·13	10·5	90·9	89·5
6	H_3PO_4*	0·00		0·00	9·32	10·4	90·7	89·6

* Compound marked with ^{32}P.

has described conditions permitting a good separation. With conditions for precipitating phosphomolybdate the same as in experiment 12, except that the solution contained 20 mg of ^{32}P-pyrophosphate instead of MBP, solutions were allowed to stand for various times. It was found that if the solution were allowed to stand for 3 hr in routine separations, <1 per cent of pyrophosphate ^{32}P would be present in the precipitate.

To estimate pyrophosphate + metaphosphate + hypophosphate advantage was taken of the fact that these compounds are converted to orthophosphate on boiling with nitric acid.[13] The filtrate from molybdate precipitation of orthophosphate as described above was made 1 M in HNO_3 and boiled for 15 min, after which orthophosphate was reprecipitated with molybdate. Under these conditions it was to be expected that orthophosphite would only partially be converted to orthophosphate since this acid is reported as being difficult to oxidize with nitric acid.[14] To check this point, 0·12 M solution of orthophosphorous acid was made 1 M in HNO_3 and boiled for 15 min, after which molybdate reagent was added. The precipitate corresponded to about 1 per cent of the orthophosphorous acid. Similarly a 0·11 M solution of hypophosphite was made 1 M in HNO_3 and boiled for 15 min. The orthophosphate precipitated from this solution corresponded to only 2–3 per cent of the hypophosphite so that hypophosphite activity is not included significantly in the precipitate at this stage. The failure to precipitate orthophosphate after treatment with nitric acid is

[11] W. F. HILLEBRANDT and G. E. F. LUNDELL, *Applied Inorganic Analysis* p. 61. John Wiley, New York (1953).
[12] L. T. JONES, *Industr. Engng. Chem. (Analyt.)* **14**, 536 (1940).
[13] J. W. MELLOR, *Comprehensive Treatise on Inorganic and Theoretical Chemistry* VIII, pp. 976, 980 and 930. Longmans Green, London (1953); R. KLEMENT, *Handbuch der Analytische Chemie* (Edited by W. FRESENIUS and G. JANDER) III, Part V, p. 306. Springer-Verlag, Berlin (1953); S. K. HAGEN, *Ibid.* II, Part V, p. 227. Springer-Verlag, Berlin (1956);
[14] S. K. HAGEN, *Ibid.* II, Part V a/b p. 227. Springer-Verlag, Berlin (1956).

TABLE 3.—PRECIPITATION OF ORTHOPHOSPHATE WITH AMMONIUM MOLYBDATE IN THE PRESENCE OF MBP (FINAL VOLUME OF EACH SOLUTION 100 ml)

(1) Experiment no.	(2) Total H_3PO_4 used (mg)	(3) Total MBP used (mg)	(4) Vol. of ammonium molybdate solution[11] (ml)	(5) Procedure	(6) Total activity in phospho-molybdate precipitate (%)
7	20*	20	36	Allowed to stand at room temperature for 20 hr after mixing together contents of columns 2, 3 and 4, and diluting to 100 ml.	>99·3
8	20	20*	36	Allowed to stand at room temperature for 20 hr after mixing together contents of columns 2, 3 and 4, and diluting to 100 ml.	10·0
9	0	20*	10	20 mg MBP* dissolved in 80 ml H_2O, 10 ml $(NH_4)_2MoO_4$ solution added, allowed to stand 10 min, diluted to 100 ml with H_2O allowed to stand 20 hr.	6·4
10	2* + 4	20	10	2 mg H_3PO_4* + 20 mg MBP in 80 ml H_2O heated to 40–50°C, 8 ml molybdate solution added; after 10 min mixing allowed to cool 1 hr, this process repeated twice with two further portions of H_3PO_4; 2 ml molybdate solution added, diluted to 100 ml with H_2O and allowed to stand 20 hr.	>98·6
11	6	20*	10	2 mg H_3PO_4* + 20 mg MBP in 80 ml H_2O heated to 40–50°C, 8 ml molybdate solution added; after 10 min mixing allowed to cool 1 hr, this process repeated twice with two further portions of H_3PO_4; 2 ml molybdate solution added, diluted to 100 ml with H_2O and allowed to stand 20 hr.	3·2
12	6	20*	10	As in 10 and 11, but allowed to stand 3 hr.	5·0

* Compound marked with ^{32}P.

perhaps to be explained by the fact that hypophosphite is first oxidized to orthophosphite which as seen above is difficult to oxidize further.

As an alternative to precipitation of orthophosphate with ammonium molybdate, magnesia mixture was used to precipitate magnesium ammonium phosphate from the alkaline extract of the irradiated TBP. Twenty millilitres of solution were neutralized to methyl red with 1 M HCl, and 20 ml of 0·4 M $BaCl_2$ added. After 30 min 5 mg each of $Na_4P_2O_6$, $K_4P_2O_7$ and $(NaPO_3)_4$ were added, and after a further 30 min similar amounts of these carriers were again added to the solution. After 60 min the precipitate was filtered off. Ten millilitres of magnesia mixture[11] were added to the filtrate, and the solution neutralized to methyl red with 2 M NH_4OH. After 30 min 10 ml of concentrated ammonia were added and then at hourly intervals two further portions of 10 mg each of H_3PO_4

[11] W. F. HILLEBRANDT and G. E. F. LUNDELL, *Applied Inorganic Analysis* p. 62. John Wiley, New York (1953).

were added. The precipitate was filtered off after 20 hr, washed five times with small portions of 0·03 M NH_4OH, dissolved in 2 M HCl and made up to 100 ml for activity estimation.

To precipitate the barium salt of hexametaphosphoric acid[16] to 25 ml of a solution containing 0·1 mg/ml of carrier MBP, DBP, orthophosphate, hypophosphate, orthophosphite, trimetaphosphate and hexametaphosphate there were added, after neutralization to methylorange, 0·5 ml 1 M HCl and 20 ml of 0·4 M $BaCl_2$. After shaking well, a further portion of 5 mg of hexametaphosphate in 0·5 ml water were added. After shaking for 5 min this operation was repeated. After standing for 15 min the precipitate was filtered off, washed five times with 0·004 M $BaCl_2$, dissolved in hot 2 M HNO_3 and the solution boiled for 15 min to convert to orthophosphate for activity estimation.

In order to separate pyrophosphate together with hypophosphate, the filtrate from the barium precipitation of hexametaphosphate, described above, was neutralized with NaOH, 3 ml of glacial acetic acid added, then 5 ml of 0·24 M sodium acetate, and the buffered solution brought to the boil. Ten millilitres of 0·4 $BaCl_2$ were then added, the solution allowed to stand for 30 min then 5 mg of carrier $Na_4P_2O_6$ and 5 mg $K_4P_2O_7$ added as carrier. After standing for 30 min, the operation was repeated. The solution was then left to stand for 60 min, after which the precipitate was filtered off, washed with 0·004 M $BaCl_2$, dissolved in 2 M HNO_3, boiled, filtered, the filter paper washed with 2 M HNO_3, and the combined filtrate and washings made up to 100 ml for activity estimation.

Reduction of orthophosphite and hypophosphite to phosphine with nascent hydrogen was examined as a method of separating the activity of these fractions from the alkaline extract of irradiated TBP after acidification. From the literature orthophosphorous acid is incompletely reduced to phosphine by zinc metal and acid.[14] DAHL, however, claims that the reduction is quantitative.[17] To check this point orthophosphite labelled with ^{32}P was prepared. To 3–300 ml of solution, in the range 0·016–0·15 M in this product, were added analytical grade zinc metal and 10–20 ml of concentrated hydrochloric acid in an apparatus similar to that described by DAHL. Repeated trials with reduction times from 1 to 2 hr showed that in our hands reactions in the temperature range 32–80°C gave less than 1 per cent of the ^{32}P in the contents of the silver nitrate traps. Even use of the apparently more effective ammoniacal solution of silver nitrate as a trapping agent for phosphine[18] did not increase this percentage. Furthermore there was an inappreciable loss of activity from the reaction flask. The ^{32}P-orthophosphite used had been prepared by hydrolysis of $^{32}PCl_3$ in carbon tetrachloride with water,[20] and the authenticity of the product was checked by absence of precipitation with molybdate reagent, and by reduction of silver nitrate to metallic silver. After the attempted reduction with zinc and hydrochloric acid the contents of the flask still gave no precipitate with molybdate reagent after heating to 45°C.

The reduction of hypophosphite was checked as follows. To 200 ml of a 0·005 M solution of sodium hypophosphite was added 20 g of analytical grade zinc and 20 ml of 9 M sulphuric acid in an apparatus similar to that of DAHL, but using a 0·02 M $AgNO_3$ solution, 0·7 M in NH_4OH in the traps. Reduction was done at 35°C for 2 hr. The black precipitate in the traps was dissolved in nitric acid, the solution boiled, and orthophosphate determined gravimetrically by precipitation with molybdate. The phosphorus in the traps corresponded to ca. 9% reduction of the hypophosphite.

^{32}P-labelled MBP and DBP submitted to reductions in the above fashion in solutions 0·016–0·30 M in the case of MBP and 0·017–0·11 M in the case of DBP gave no appreciable activity in the silver nitrate traps. Similarly 0·03–0·04 M solutions of ^{32}P-hypophosphate showed no appreciable reduction.

Thus it was concluded that reduction carried out as described above in the case of hypophosphite would yield evidence of presence of this compound in the alkaline extract of irradiated TBP, free from any accompanying activity from orthophosphorous acid, hypophosphoric acid, MBP or DBP despite the relatively low efficiency of reduction of the hypophosphite. On the other hand elementary phosphorus, if present in the alkaline extract, could contribute to the activity of the phosphine liberated in this reduction, since white phosphorus is known to be reduced in these conditions.[19]

The ^{32}P-labelled phosphorus acids for the above experiments were prepared by appropriate

[16] R. KLEMENT, *Handbuch der Analytische Chemie* (Edited by W. FRESENIUS and G. JANDER) III, Part V, p. 313. Springer-Verlag, Berlin (1953).
[17] J. B. DAHL, *JENER* Report 40 (1956).
[18] S. K. HAGEN, *Handbuch der Analytische Chemie* (Edited by W. FRESENIUS and G. JANDER) II, Part V, p. 200. Springer-Verlag, Berlin (1956).
[19] S. K. HAGEN, *Handbuch der Analytische Chemie* (Edited by W. FRESENIUS and G. JANDER) II, Part V, p. 213. Springer-Verlag, Berlin (1956).

methods: ^{32}P-orthophosphite, ^{32}P-hypte,[20] ^{32}P-pyrophosphaophosphate,[21] and these methods were also used to prepare non-labelled carriers. Non-labelled carriers of trimetaphosphate, hexametaphosphate[22] were also prepared. Commercially available hypophosphite was used as carrier for this form.

RESULTS

Results of irradiations are shown in Table 4. The pile irradiations were done under the following conditions:

Analysis	Condition of pile
1	Thermal column JENER reactor, $\sim 10^9$ neutrons cm^{-2} sec^{-1}, 144 hr, analysed 10 days after irradiation.
2*	Thermal column JENER reactor, $\sim 10^9$ neutrons cm^{-2} sec^{-1}, 144 hr, analysed 10 days after irradiation.
3	Thermal column "EWA", $\sim 9 \times 10^{10}$ neutrons cm^{-2} sec^{-1}, 6 hr, analysed 6 days after irradiation.
4	Thermal column "EWA", $\sim 9 \times 10^{10}$ neutrons cm^{-2} sec^{-1}, 6 hr, analysed 6 days after irradiation.
5	Thermal column "EWA", $\sim 9 \times 10^{10}$ neutrons cm^{-2} sec^{-1}, 6 hr, analysed 16 days after irradiation.
6	Thermal column "EWA", $\sim 9 \times 10^{10}$ neutrons cm^{-2} sec^{-1}, 6 hr, analysed 16 days after irradiation
7	Thermal column "EWA", $\sim 9 \times 10^{11}$ neutrons cm^{-2} sec^{-1}, 48 hr, analysed 9 days after irradiation.
8	Thermal column "EWA", $\sim 9 \times 10^{11}$ neutrons cm^{-2} sec^{-1}, 48 hr, analysed 9 days after irradiation.
9	Thermal column "EWA", $\sim 9 \times 10^{11}$ neutrons cm^{-2} sec^{-1}, 48 hr, analysed 26 days after irradiation.
10	Thermal column "EWA", $\sim 9 \times 10^{11}$ neutrons cm^{-2} sec^{-1}, 48 hr, analysed 26 days after irradiation.

* In this analysis, the alkaline extract of irradiated TBP was extracted first with amyl alcohol and then with benzene, whereas in the other analyses extraction was done first with benzene, then with amyl alcohol.

DISCUSSION

It is assumed on the basis of careful previous work[23] that no isotope exchange occurs between any of the inorganic compounds of phosphorus here examined.

A complicated spectrum of γ-rays is emitted from phosphorus after neutron capture.[24] In order to calculate approximate probabilities of total escape of the hot ^{32}P atom from its initial bonds in TBP by appropriate stochastic procedure,[25] two fairly probable cases of serial quantum emission have been assumed:

(1) Serial emission of three of the observed quanta of 2·19 MeV, the residue of 1·37 MeV of the available 7·94 MeV neutron binding energy being neglected and

(2) Serial emission of two of 2·19 MeV quanta followed by emission of a 3·55 MeV quantum, summing to 7·93 MeV.

[20] A. Siuda, Institute of Nuclear Research, Warsaw, Report 40/*V* (1958).
[21] R. N. Bell, *Inorganic Synthesis* (Edited by L. F. Audrieth) Vol. 3, p. 100, McGraw-Hill, New York (1950).
[22] R. N. Bell, *Inorganic Synthesis* (Edited by L. F. Audrieth) Vol. 3, p. 103. McGraw-Hill, New York (1950).
[23] N. J. Wilson, *J. Amer. Chem. Soc.* **60**, 2697 (1938); D. Hull, *J. Amer. Chem. Soc.* **63**, 1269 (1941); W. P. Ionin, A. F. Lukovnikov, N. B. Neoman and A. N. Nesmeianov, *Dokl. Acad. Nauk SSSR* **67**, 463 (1949).
[24] G. A. Bartholomew and L. A. Higgs, *Compilation of Thermal Neutron Capture Gamma Rays* p. 25. AECL No. 669, CRGP-784 Atomic Energy of Canada Ltd. (1958).
[25] J. W. Cobble and G. E. Boyd, *J. Amer. Chem. Soc.* **74**, 1282 (1952); I. G. Campbell, *Nukleonika* **2**, 605 (1957).

TABLE 4.—DISTRIBUTION OF ^{32}P ACTIVITY IN FRACTIONS OF IRRADIATED TBP

(a) Substances	(b) Separation procedure	Total activity in fraction (%)											
		(c) 1st irradiation with Ra/Be	(d) 2nd irradiation with Ra/Be	(e) Pile irradiation 1st analysis	(f) Pile irradiation 2nd analysis	(g) Pile irradiation 3rd analysis	(h) Pile irradiation 4th analysis	(i) Pile irradiation 5th analysis	(j) Pile irradiation 6th analysis	(k) Pile irradiation 7th analysis	(l) Pile irradiation 8th analysis	(m) Pile irradiation 9th analysis	(n) Pile irradiation 10th analysis
1. Phosphine	Flushed out of ampoule with phosphine carrier	—	—	≤0·01	—	≤0·001	—	—	—	≤0·0001	—	—	—
2. TBP (+ unknown compounds?)	Activity remaining in TBP after extraction	5·3	5·0	5·5 5·4 5·6 5·6	5·4 5·5 5·4 5·4	31·0	31·0	27·6	27·7	68·0	67·8	59·0	59·1
3. All substances extractable with NaOH	NaOH extract	—	—	94·0 93·8	93·6 90·4	—	—	—	—	—	—	—	—
4. DBP (+ unknown compounds?)	Benzene extract	22·2	25·9	28·5 28·2	—	27·0	27·4	28·4	28·4	21·0	21·1	24·0	24·1
5. MBP plus small proportion of inorganic P acids (+ unknown compounds?)	*n*-Amyl alcohol extract	35·8 (pH 0·38 in aq. phase)	33·5 (pH 0·70)	31·4 (pH 0·30) 31·7 (pH 0·29)	64·7 (pH 0·31) 64·9 (pH 0·30)	25·7 (pH 0·56)	25·7 (pH 0·60)	25·7 (pH 0·51)	25·4 (pH 0·55)	6·7 (pH 0·70)	6·7 (pH 0·52)	11·4 (pH 0·49)	11·7 (pH 0·56)
6. Inorganic P acids, less small fraction extracted with amyl alcohol, plus small amount of non-extracted MBP	Aqueous phase after benzene and amyl alcohol extracts	36·6	35·5	30·2 30·2	25·5 27·5	14·4	14·4	14·8	15·7	2·8	2·8	3·2	3·1
7. Orthophosphate	Precipitate with ammonium molybdate from aqueous phase after benzene and amyl alcohol extraction	—	—	13·3 13·7	11·5 12·5	6·2	5·3	4·5	4·6	0·4	0·5	1·1	1·4
8. Orthophosphate	Precipitate with ammonium molybdate from alkaline extract of TBP	—	—	15·7	16·2	—	—	—	—	—	—	—	—
9. Orthophosphate	Precipitate with magnesia mixture from alkaline extract of TBP	—	—	11·7	11·7	—	—	—	—	—	—	—	—
10. Hexametaphosphate	Precipitation with Ba at low pH from alkaline extract of TBP	—	—	2·0 1·8	1·1 1·1	—	—	—	—	—	—	—	—
11. Hypophosphate + pyrophosphate	Precipitate with Ba in buffered filtrate from hexametaphosphate precipitation (fraction 10)	—	—	—	1·1 1·1	—	—	—	—	—	—	—	—
12. Pyrophosphate + metaphosphate + hypophosphate	Difference between activity precipitate with molybdate after 15 min boiling with 1 M HNO_3 and activity precipitated in cold with molybdate	—	—	4·3 3·2	2·3 3·2	0·0	0·0	0·0	0·0	0·2	0·1	0·0	0·0
13. Hypophosphite (+ elementary P?)	Reduction with nascent hydrogen	— —	—	≤2	≤2	—	—	—	—	—	—	—	—
14. Orthophosphite	Filtrate after molybdate precipitation 7 boiled with 1 M HNO_3 for 15 min, then orthophosphate reprecipitated as in 7	—	—	12·6 13·3	11·7 11·8	9·1	9·1	10·3	11·2	2·2	2·2	2·1	2·0

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Assuming 25 eV as the total binding energy of phosphorus-oxygen bonds in TBP,[26] calculations show that in case (1) 3·5 per cent and in case (2) 2·2 per cent of the ^{32}P daughter atoms should fail to escape from TBP. Such a low percentage is to be expected in view of the relatively large weight of the molecular residue. Serial emission of more than three quanta of lower energies from the compound nucleus would increase the primary retention due to failure to rupture bonds, but such emission schemes are presumably less probable. Thus the total of ca. 65 per cent of ^{32}P activity in organic combination in the TBP, benzene and amyl alcohol fractions in the case of Ra/Be irradiations or pile analyses 1 and 2 in Table 4 for example, must be due in overwhelming degree to processes other than primary retention.

From Table 4 it can be seen that Ra/Be source irradiation and reactor thermal column irradiation at 10^9 neutrons cm^{-2} sec^{-1} lead to approximately 5·5 per cent of the ^{32}P activity being retained in the TBP in a form not extractable with NaOH solution. Presumably this activity is present largely as $TB^{32}P$.

It can also be seen that Ra/Be irradiation and irradiation at 10^9 neutrons cm^{-2} sec^{-1} lead to 22–28 per cent of activity being retained in organic combination, in a form extractable by benzene, which would contain any TBP formed, and may contain other compounds, and ca. 33 per cent of activity being retained in a form extractable by amyl alcohol, containing the major part of any MBP formed and possibly other organic compounds. Approximately 26–36 per cent of the ^{32}P activity is present in inorganic form at these levels of irradiation.

It is interesting to compare these results with those obtained by MADDOCK and SUTIN[3] for the irradiation of triphenylarsine, in which about 9 per cent of activity was present as Ph_3As, 13 per cent as Ph_2As, 35 per cent as PhAs and 31 per cent as inorganic As. This is similar general pattern to that obtained in our experiments, in that formation of bonds between neutron activated atom and three organic residues is least probable, formation of bonds with two residues being more probable, and formation of a bond with a single organic residue being about as probable as formation of no such bond. An important difference between the two systems is that in the case of naked ^{76}As atoms, direct formation of phenyl compounds can occur by formation of a As—C bond with an organic radical, whereas in our case, naked ^{32}P atoms could combine to form esters either in a one-step reaction with oxygen-containing organic products (alcohols) or in two-step process involving first the formation of phosphorus oxy-acids, possibly excited, and then esterification.

Apart from the formation of P—O—C bonds it is also possible that P—C bonds could arise as a result of reaction of ^{32}P atoms directly with organic radicals. Such compounds might in part undergo hydrolysis during alkaline extraction of the irradiated TBP, and in this case the ^{32}P recovered in organic form would partly represent a secondary product. It is also conceivable that some compounds having P—C bonds could resist hydrolysis, and could either remain in the TBP after alkaline extraction, or if possessing acidic functions, be extracted into aqueous phase, from which they could subsequently be removed by benzene or amyl alcohol extractions. It is clear that the benzene and amyl alcohol fractions can in no way be treated as representing solely MBP or DBP, and their composition must be the subject of subsequent work.

[26] B. P. NIKOLSKI, *Spravocnik Chimika* Vol. 1, p. 276. G.H.I., Moscow (1951).

It is also interesting to compare our results with the work of ERBACHER and PHILIPP on neutron irradiation of triphenyl phosphate with a Ra/Be source.[8] These authors found that irradiation of triphenyl phosphate in benzene leads to production of 40 per cent of total activity extractable with pure water. This should correspond to the inorganic P fraction in our experiments, since monophenyl phosphate and diphenyl phosphate will probably have small coefficients of partition into water from benzene solutions. Their percentage agrees well with our figure of 36 per cent for this fraction in Ra/Be irradiations.

The effect of increasing the intensity of irradiation on the distribution of activity is very marked in our experiments. As irradiation level is increased from 10^9 to 9×10^{10} neutrons cm^{-2} sec^{-1} the activity remaining in TBP increases from 5·5 to 31 per cent and further increase of irradiation intensity to 9×10^{11} leads to the remarkable figure of 68 per cent of activity being present as a fraction not extractable from TBP with NaOH. That this is not a monolithic fraction is shown by the fact that allowing the sample to stand for some days after irradiation and before alkaline extraction leads to a loss of 3 per cent of activity from this extraction fraction in the case of irradiation at 9×10^{10} neutrons cm^{-2} sec^{-1} and loss of 9 per cent of activity in the case of irradiation at 9×10^{11} neutrons cm^{-2} sec^{-1}. From Table 4 it would seem that the loss of activity from the TBP fraction on allowing to stand in the case of the irradiation done at 9×10^{11} neutron cm^{-2} sec^{-1} appears to occur with a simultaneous increase in the fraction extractable with amyl alcohol.

From Table 4 it appears that increase in the TBP fraction with increasing intensity of irradiation is accompanied by a small reduction in the benzene fraction and a marked reduction in the amyl alcohol and inorganic fractions. At higher dose intensities gamma induced radiolysis of the TBP will be more pronounced, and in particular, the concentration of butyl radicals and butyl alcohol in the medium will rise. BURR[27] has shown that butane and butene are prominent in the products of radiolysis of TBP by electrons, and BURGER and MCCLANAHAN[28] have shown that butyl alcohol is formed during γ-irradiation. This effect is being further examined, but at this stage it is suggested as a preliminary hypothesis that a ^{32}P atom has a greater chance of forming tributyl derivatives by recombination in a medium rich in butyl radicals or butyl alcohol, and that this radiation promoted synthesis takes place at the expense of the amyl alcohol fraction and inorganic ^{32}P compounds.

In any case the existence of such a radiation effect indicates that at irradiation levels higher than 10^9 neutrons cm^{-2} sec^{-1}, the "billiard ball" collision mechanism of LIBBY[6] cannot fully explain the retention of ^{32}P in the TBP fraction, and suggests most strongly that radical mechanism play an important role at these dose rates. One would theoretically expect no strong dependence of retentions on the neutron irradiation intensity on the basis of a collision type mechanism, and if this were the only or mainly effective mechanism leading to retention one would also not expect a strong dependence on rate of radical formation. On the other hand no evidence can be adduced as to the role of radical mechanisms at irradiation intensities below 10^9 neutron cm^{-2} sec^{-1}. In fact the general agreement between the distribution of ^{32}P between the TBP, benzene, amyl alcohol and inorganic fractions in the case of Ra/Be irradiation and irradiation at 10^9 neutron cm^{-2} sec^{-1}, suggests that at the latter

[27] I. G. BURR, *Rad. Res.* **8**, 214 (1958).
[28] L. L. BURGER and E. D. MCCLANAHAN, *Industr. Engng. Chem.* **50**, 153 (1958).

intensity of irradiation the system is still independent of the rate of radical formation by radiolysis.

The increase in percent activity in the TBP fraction as irradiation level is increased to 9×10^{11} neutron cm^{-2} sec^{-1} seems to be too large to be explicable on the basis of the undoubtedly increased participation of fast neutrons in the total neutron dose at this level, although the $^{31}P(n, \gamma)^{32}P$ reaction cross-section does show a multiplicity of peaks in the region up to 1 MeV neutron energy.[29]

With regard to the inorganic forms of phosphorus, it can be seen that orthophosphite is present as 9–13 per cent of total ^{32}P activity, but that hexa- and trimetaphosphate, pyrophosphate, hypophosphate and hypophosphite do not seem to be present in very significant amounts. It is interesting to note that when irradiation is done at a level of 10^9 neutron cm^{-2} sec^{-1}, the amount of ^{32}P present as 5+ in the inorganic fraction is approximately equal to that present as 3+ in orthophosphite. LIBBY found a similar ratio in neutron irradiated inorganic phosphates[30] and concluded that in approximately 50 per cent of events the recoil ^{32}P was present as 5+ and in 50 per cent of events as 3+, the chemical environment being unable greatly to influence the oxidation number with which the phosphorus was finally stabilized. If the chemical environment were similarly unable to oxidize $^{32}P^{3+}$ to $^{32}P^{5+}$ in the case of neutron irradiated TBP, and no P^{3+} organic compounds were formed, it would follow that as a result of the primary neutron event 9–13 per cent of the ^{32}P atoms were formed as P^{3+}, finishing their career as PO_3^{3-}, and 91–87 per cent as P^{5+}, finishing their career as organic esters, orthophosphate, and to a small extent as metaphosphate and pyrophosphate. This would be in disagreement with the results of irradiating solid orthophosphate crystals and orthophosphate solutions by LIBBY, quoted above, and also with similar results on irradiation of orthophosphate crystals obtained by ATEN *et al.*[31] In the case of TBP either the division of bonding electrons between oxygen and departing hot ^{32}P atoms is different from that in neutron irradiated inorganic orthophosphates, or $^{32}P^{3+}$ atoms have an appreciable probability of being oxidized in an environment of irradiated TBP, or can perhaps undergo exchange reactions with P^{5+} compounds in this system; or some of the ^{32}P in organic combination is present as 3+ (e.g. esters of orthophosphorous acid). It should be pointed out, in addition, that SELLERS *et al.*[32] on the basis of irradiation of carefully degassed crystalline orthophosphate at 10^{13} neutron cm^{-2} sec^{-1} found no evidence of orthophosphite among the radiation products, and in fact it would appear from their experiments that at high level irradiation *in vacuo* all ^{32}P atoms finish their career in the 5+ state.

In our experiments no ^{32}P was found in the 3− state as PH_3. Nothing can be said as to presence of elementary phosphorus on the basis of the present data.

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[29] D. J. HUGHES and R. B. SCHWARTZ, *Neutron Cross Sections* (2nd Ed.) p. 126. BNL-325 (1958).
[30] W. F. LIBBY, *J. Amer. Chem. Soc.* **62**, 1930 (1940).
[31] A. H. W. ATEN, JR., H. VAN DER STRAATEN and P. C. RIESEBOS, *Science* **115**, 267 (1952).
[32] P. A. SELLERS, T. R. SATO and H. H. STRAIN, *J. Inorg. Nucl. Chem.* **5**, 31 (1957).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 238 to 249. Pergamon Press Ltd. Printed in Northern Ireland

A LAMELLAR COMPOUND OF SODIUM AND GRAPHITE

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Abstract—A previously unknown compound of sodium and graphite, having an ideal formula $C_{64}Na$ is described. It has a lamellar structure in which sodium is intercalated in every eighth interplanar gap and appears to be analogous to the K–, Rb– and Cs– graphite lamellar compounds. The main evidence for its existence and structure is from X-ray diffraction studies, supported by magnetic susceptibility determinations and measurements of the dilation occurring when graphite is immersed in sodium.

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COMPOUNDS of the alkali metals, potassium, rubidium and caesium, with graphite are well known.[1,2,3,4,5] However, any corresponding sodium–graphite compounds have been believed to be non-existent since attempts to prepare them have been unsuccessful.[1,2,4] Moreover, both UBBELOHDE[6] and HENNIG[7] have given thermodynamic reasons why they should be less stable than the K–, Rb–, and Cs–compounds.

The present work provides evidence that at least one sodium–graphite lamellar compound exists although its stability is low. This was first suggested, although not unequivocally, by studies[8] on the compatibility of sodium and graphite and on the contact angle between them, carried out in connexion with sodium-cooled graphite-moderated nuclear reactors. In this paper are described experiments which confirm this hypothesis.

The main technique used was X-ray diffraction which, of course, directly indicates changes in the lattice structure. Supporting evidence was obtained from the determination of the magnetic susceptibility, because of its dependence on electronic band structure, and from measurements of the dilation which, as reported by previous authors,[9,10,11] occurs when graphite is immersed in sodium.

EXPERIMENTAL

Materials

Sodium. Unless otherwise stated commercial sodium was used and filtered at about 150°C through sintered glass disks (porosity 3 or 4) to remove solid impurities.[12] Its potassium content was about 100–130 p.p.m.[13]

For one experiment the potassium content was reduced by a method based on that suggested by

[1] K. FREDENHAGEN and G. CADENBACH, *Z. Anorg. Chem.* **158**, 249 (1926).
[2] K. FREDENHAGEN and M. SUCK, *Z. Anorg. Chem.* **178**, 353 (1929).
[3] A. HÉROLD, *Bull. Soc. Chim.* 999 (1955).
[4] A. SCHLEEDE and M. WELLMAN, *Z. Phys. Chem.* **B 18**, 1 (1932).
[5] W. RUDORFF and E. SCHULZE, *Z. Anorg. Chem.* **277**, 156 (1954).
[6] F. R. M. MCDONNELL, R. C. PINK and A. R. UBBELOHDE, *J. Chem. Soc.* 191 (1951).
[7] G. R. HENNIG, *Proceedings of the Conferences on Carbon* p. 103. University of Buffalo (1955).
[8] R. C. ASHER, AERE/CE/R-2618 (1958).
[9] S. SIEGEL, R. L. CARTER, F. E. BOWMAN and B. R. HAYWARD, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1955, p. 829. United Nations (1956).
[10] T. A. COULTAS and R. CYGAN, NAA-SR-258 (1953). Declassified (1957).
[11] A. B. MARTIN and J. C. COCHRAN, NAA-SR-1582 (1956). Declassified (1957).
[12] M. SITTIG, *Sodium, Its Manufacture, Properties and Uses.* Reinhold, New York (1956).
[13] R. T. BIRKS, Chemistry Division, A.E.R.E. Private communication (1958).

RUEBSAMEN[14] and which relies on the reaction of even traces of potassium with graphite. About 20 g of filtered sodium was heated with 1–2 g powdered reactor grade graphite (less than 60 mesh) for about 10 hr at 400°C in a stainless steel crucible. The purified sodium was separated by decantation; analysis by flame photometry showed 50 p.p.m. of potassium.[15]

For the magnetic susceptibility measurements the sodium was prepared by an electrolysis technique described below.

Graphites. Four powders and five artefacts were studied.

The *powders* selected covered a range of crystallite sizes, characterized by the values of p; p is the probability of a stacking fault occurring in the crystal lattice at a given interplanar gap and it was evaluated from the broadening of the 1122 X-ray diffraction line. The powders were:

A Highly crystalline artificial graphite $p = 0{\cdot}02$
B Natural graphite $p = 0{\cdot}03$
C Reactor grade graphite $p = 0{\cdot}15$
D Petroleum coke calcined at 2000°C, $p = 0{\cdot}4$

The *artefacts* were chosen to cover a range of thermal expansion coefficients (see Table 4) and were:

I, II, III and IV Fairly conventional electrographite artefacts of which (I) is reactor grade graphite.
V Hydrostatically-pressed powdered reactor grade graphite.

X-ray diffraction studies

X-ray diffraction studies were made on mixtures of various proportions of sodium and graphite prepared under a range of thermal conditions in a "glove-box" containing continuously purified helium (oxygen content less than 10 p.p.m.). In a typical preparation 5 g of powdered graphite was dried at 400°C in a stainless steel crucible, the required weight of sodium added and the heating continued for a further 0·5 hr with stirring. When cool, a few milligrammes of the material were placed in a silica quill tube (0·5–1·0 mm diameter) and the open end sealed with vacuum wax. The sample, thereby protected from the air, was removed from the glove box and its X-ray diffraction photograph obtained in the usual way using Cu$K\alpha$ radiation; the walls of the quill tube were thin enough (3μ) to be transparent to X-rays.

Magnetic susceptibility measurements

Sealed capsules containing known amounts of sodium and graphite were made by a method illustrated in Fig. 1(a) and based on the mobility of sodium ions in hot soda glass.[16] Sodium ions are transported electrolytically from the molten sodium nitrite (300–350°C) through the glass and are deposited quantitatively[16] as metallic sodium in contact with the graphite cathode. In the present experiments 1–10 mA was passed for 0·5–4 hr. After the electrolysis, the wire was withdrawn, the glass sealed at *A*, the sample heated at 400°C for 0·5 hr (in the hope of promoting any sodium–graphite interaction) and the susceptibility measured; allowance was made for the contribution of the glass, based on a subsequent measurement on the empty capsule.

To minimize errors due to ferromagnetic impurities, the graphite was previously passed through a magnetic separator.

The susceptibility of the sodium itself was measured to check the absence of impurities of high susceptibility. A modified apparatus (Fig. 1b) was used to prepare the sample since in the absence of the graphite it was difficult to make electrical contact between the wire and the glass. The procedure adopted was to distil the sodium produced in bulb *B* into bulb *C*, withdraw the wire and seal the glass at *D* and *E*. This sodium had a susceptibility of $+0{\cdot}15 \pm 0{\cdot}15$ c.g.s. units g^{-1}, which is in reasonable agreement with the literature[17] figure ($+0{\cdot}68 \times 10^{-6}$ c.g.s. units g^{-1}), and contained 700 p.p.m. potassium.[15]

Extensometric measurements of the dilation

The apparatus used for measuring the total dilation of various graphites in contact with sodium is shown in Fig. 2 which is self explanatory. The sodium was contacted with the graphite, the

[14] W. C. RUEBSAMEN, NAA-SR-139 (1951).
[15] J. C. COTTERILL, A.E.R.E., Woolwich Outstation. Private communication (1958).
[16] R. C. BURT, *J. Optical Soc. Amer.* **11**, 87 (1925).
[17] P. W. SELWOOD, *Magnetochemistry*. Interscience, New York (1943).

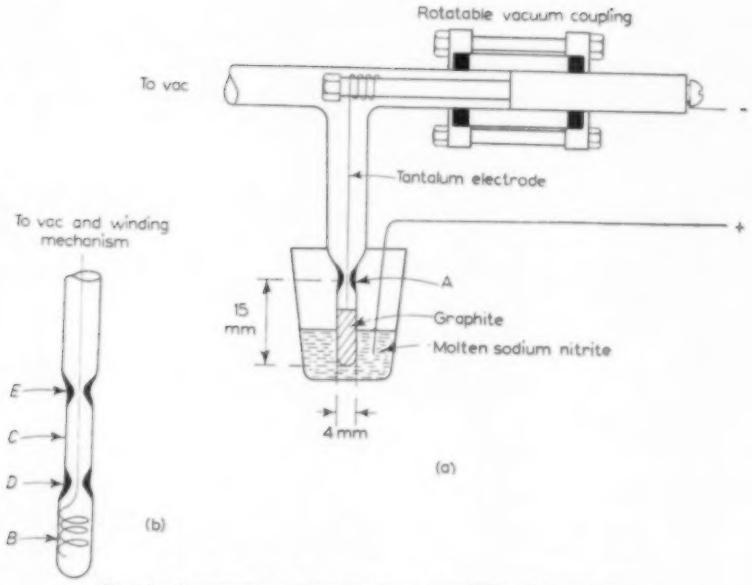

FIG. 1.—Preparation of samples for susceptibility determinations.

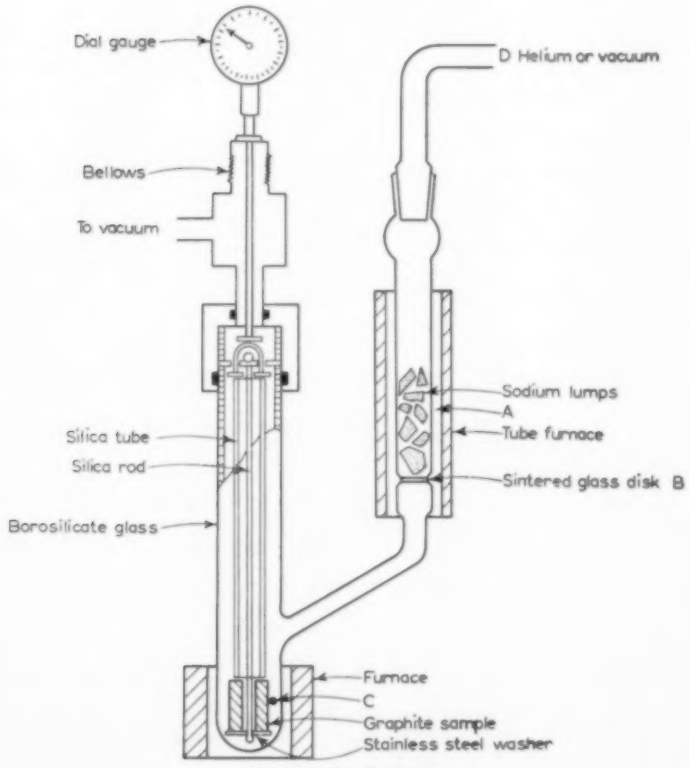

FIG. 2.—Extensometer.

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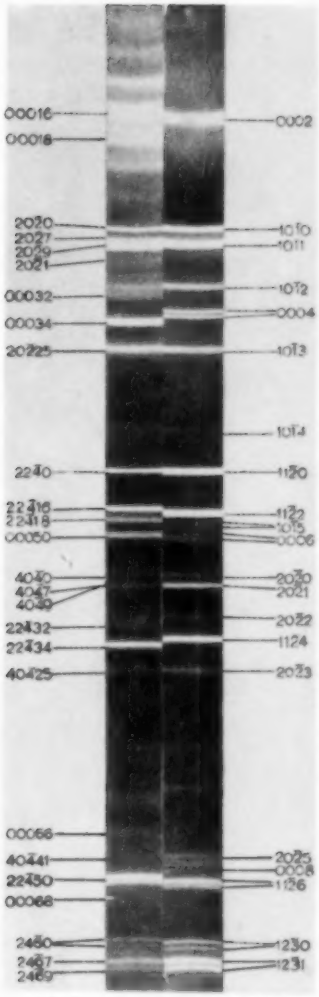

(a) (b)

FIG. 3.—X-ray diffraction photographs of natural graphite (a) before and (b) after treatment with sodium.

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temperature raised (at 150°C per hr) to 400°C where it was maintained until no further dilation was indicated. The dilation appeared to be complete under these conditions since on raising the temperature a further 40°C no additional dilation occurred. Errors due to the thermal expansion of the apparatus are negligible since the important components were made of silica.

RESULTS

X-ray diffraction

X-ray diffraction photographs of Graphite B before and after treatment with sodium are given in Figs. 3(a) and 3(b). Similar photographs were given by Graphites A, C and D, although the last two, which are less crystalline than Graphite B gave

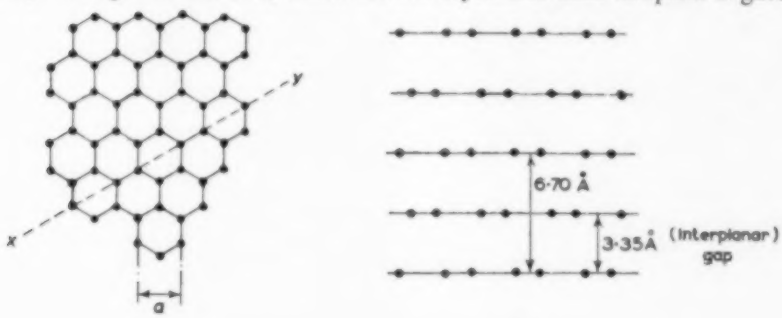

FIG. 4.—Lattice structure of graphite. (a) Portion of graphite sheet, (b) arrangement of sheets [section along XY of (a)].

broader lines; the definition was also improved by prolonged heating of the sodium–graphite preparation at about 400°C.

The detailed interpretation of the X-ray diffraction results was carried out by MR. S. WILSON, and will be reported elsewhere. Only the general implications will be discussed here.

The X-ray diffraction results provide the main evidence for (a) the chemical interaction of sodium and graphite and (b) the lamellar nature of the product.

(a) The occurrence of interaction is shown by the remarkable change in the diffraction pattern when graphite is treated with sodium. Most noticeable is the disappearance of the 0002 graphite line (cf. Figs. 3a and b). Since this line is very characteristic of graphite, a few per cent being sufficient to produce it, its disappearance means that virtually all the graphite has reacted in some way. Moreover, two separate intense lines have appeared not far from the site of the 0002 line and must also be attributed to a new compound. Several other graphite lines have disappeared in the same way as the 0002 and are replaced with new lines in different positions.

(b) The lamellar nature of the compound is clear from a consideration of the changes in the pattern. Thus, although all the graphite has reacted, an important group of lines are, as far as can be detected, unchanged in position and are at least approximately unchanged in intensity. These lines (e.g. the $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, and $12\bar{3}0$ lines) are those whose positions depend on the a spacing, that is the dimensions of the hexagons in the graphite sheets (Fig. 4a). Therefore the structure of the graphite sheets must be unaffected. On the other hand the lines such as the 0002, which have, in fact, been displaced, are governed by the spacing between the graphite sheets, i.e. the interplanar spacing (Fig. 4b). It is clear then that compound formation

has altered the spacing between the graphite sheets but has not appreciably altered their structure. This is consistent with the formation of a lamellar compound but not, for example, of sodium carbide.*

The probable lattice structure of the compound has been deduced from the X-ray diffraction results by fairly standard procedures. Briefly, several likely lamellar structures were considered in detail and the positions and intensities of the expected diffraction lines calculated for each; a comparison of these calculated figures with

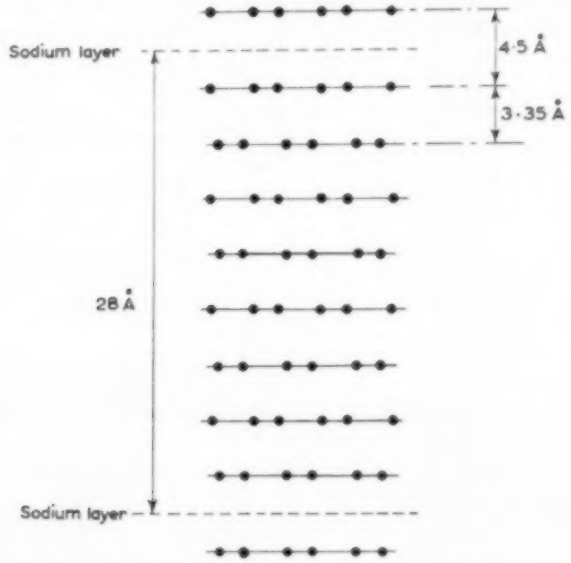

FIG. 5.—Layer lattice of sodium–graphite compound.

the experimental data revealed the most probable structure. All the other structures examined gave much worse agreement. The calculated figures for the most likely structure are compared with the experimental figures in Table 3.

The lamellar structure arrived at in this way is that in which sodium has penetrated into every eighth interplanar gap (Fig. 5). For these gaps the interplanar spacing has increased from 3·35 Å for graphite to about 4·6 Å in the compound. The remaining interplanar gaps remain unchanged. The magnitude of this increase in interplanar spacing is reasonable in view of the radius of the sodium atom (ca. 1·86 Å). The unit cell dimension in the *c* direction, viz. perpendicular to the graphite sheets, now comprises seven spacings as in graphite itself (3·35 Å) and one expanded to 4·6 Å. It is therefore 28 Å compared with 6·70 Å (i.e. $2 \times 3{\cdot}35$ Å) in graphite. The average interplanar spacing is thus $28/8 = 3{\cdot}5$ Å, an increase of about 5 per cent over that of graphite.

The X-ray diffraction results also provide evidence on the composition of the new compound. It has been found that, in the general case, whatever proportions

* Attempts were made to detect carbide formation by treating graphite with sodium, reacting the product with water and testing the gas for acetylene. Although the gas smelt faintly of acetylene, chemical methods and mass-spectrometry have failed to confirm its presence. It is believed therefore that merely traces of carbide are formed and suggested that these may be calcium carbide formed from calcium impurity (10–100 p.p.m.)[24] in the sodium.

of sodium and graphite are used in the preparation, the structure of the compound, indicated by the X-ray photograph, is always the same. In particular the interplanar spacing is constant to better than 0·1 per cent. The compound has a fairly well defined range of composition and if excess of either sodium or graphite is used, extra lines characteristic of sodium or graphite occur in the X-ray line spectra. Therefore, by studying materials containing different proportions of sodium and noting which of these gives no extra lines it is possible to ascertain the composition of the compound.

TABLE 1.—MAGNETIC SUSCEPTIBILITY RESULTS

	Sodium	Graphite C	Graphite C and 25% sodium	
			Experimental	Calc*
Susceptibility (c.g.s. units $g^{-1} \times 10^6$)	$+ 0{\cdot}15 \pm 0{\cdot}15$	$-3{\cdot}65 \pm 0{\cdot}05$	$+ 0{\cdot}40 \pm 0{\cdot}05$	$-2{\cdot}85 \pm 0{\cdot}15$

* Calculated as a physical mixture

Because of the experimental difficulty of detecting traces of excess sodium this method is imprecise but it appears certain that the composition is between $C_{53}Na$ and $C_{66}Na$. It is likely that the ideal composition is $C_{64}Na$ but that defect structures covering a range of compositions on either side of this are possible. Similar ranges of composition seem to occur in the cases of the higher alkali metal–graphite compounds. For instance, RUDORFF and SCHULZE[5] found that compositions from $C_{21{\cdot}3}K$ to $C_{27{\cdot}7}K$ all gave the diffraction pattern corresponding to the ideal formula $C_{24}K$.

Magnetic susceptibility

The susceptibility results (Table 1) also appear to be compatible with the formation of a lamellar compound. The sodium–graphite preparation cannot be a physical mixture but must have reacted chemically since its susceptibility is $0{\cdot}40 \pm 0{\cdot}05 \times 10^{-6}$ c.g.s. units g^{-1} whereas for a physical mixture $2{\cdot}85 \pm 0{\cdot}15 \times 10^{-6}$ c.g.s. units g^{-1} would be expected. The interaction thus results in a marked change from the strong diamagnetism of graphite ($-3{\cdot}65 \pm 0{\cdot}05 \times 10^{-6}$ c.g.s. units g^{-1}) to the slight paramagnetism of the compound, which therefore may be considered as 'more metallic' than graphite. A similar phenomenon was found with the well-known potassium–graphite lamellar compounds by UBBELOHDE[6] and by RUDORFF and SCHULZE[5] who give for C_8K the figures of $+ 1{\cdot}0 \times 10^{-6}$ c.g.s. units g^{-1} and of $+ 0{\cdot}6$ to $0{\cdot}7 \times 10^{-6}$ units g^{-1} respectively. Qualitatively these changes in susceptibility are not unexpected. The formation of alkali-metal lamellar compounds involves, according to HENNIG,[7,18,19] electron transfer from the metal to the giant π orbits of the graphite; it must therefore result in considerable perturbations in precisely those orbits which give rise to the high diamagnetism of graphite.[5,6,17]

[18] M. L. DZURUS and G. R. HENNIG, *J. Amer. Chem. Soc.* **79**, 1051 (1957).
[19] M. L. DZURUS and G. R. HENNIG, *J. Chem. Phys.* **27**, 275 (1957).

Dilation

The figures for the dilation in sodium for a range of materials are given in Table 2. These figures provide indirect support for the lamellar structure proposed above since the dilation can be predicted quantitatively on the reasonable assumption that it results from the increase in the interplanar spacing. The calculation is based on the fact that the graphite artefacts were polycrystalline, the crystallites having a small preferred orientation which causes anisotropy in many properties. In the

TABLE 2.—DILATION IN SODIUM

Material		Dilation %
Graphite I	∥	0·92
	⊥	0·60
Graphite II	∥	0·77
Graphite III	∥	0·36
Graphite IV	∥	0·41
	⊥	1·0
Graphite V		2·3

∥ and ⊥ indicate respectively samples cut with axes *parallel* to and *perpendicular* to extrusion direction.

extruded material the crystallities will tend to be oriented with the graphite sheets parallel to the direction of extrusion (Fig. 6a) whilst in a pressing they will tend to be normal to the pressing direction (Fig. 6b).

Consider such a polycrystalline artefact length l, schematically represented by Fig. 7. The increase in interplanar spacing of each crystallite by $\Delta_c\%$ will contribute an amount $\frac{t\Delta_c}{100}\sin\psi$ in the direction XY, t being the thickness of the crystallite, and ψ its inclination to XY. D, the percentage dilation of the artefact as a whole, is therefore,

$$D = \sum \frac{t\Delta_c \sin\psi}{l} = \frac{T\Delta_c}{l} \tag{1}$$

where T is a constant, characteristic of the graphite and the direction XY.

T is estimated from the related phenomenon of thermal expansion. The thermal expansion results from an increase in the interplanar spacing together with a small effect due to a *decrease* in the a spacing. The equation analogous to (1) is:[20]

$$\alpha = \frac{T\alpha_c + (1 - T)\,\alpha_a}{l} \tag{2}$$

where α_c, α_a and α are the linear thermal expansion coefficients for, respectively, the c direction, the a direction and the artefact as a whole. Combining (1) and (2) gives:

$$D = \Delta_c \frac{\alpha - \alpha_a}{\alpha_c - \alpha_a} \tag{3}$$

[20] I. B. MASON, AERE Report H/G/G.-24 (1956).

Within the limitations of the model this equation holds for thermal expansion data at any given temperature. In the present work average figures for α between liquid nitrogen temperature and room temperature were used; the corresponding values of α_a and α_c were estimated from the data of RILEY[21] to be $-1{\cdot}0 \times 10^{-6}$ and 18×10^{-6} respectively. Therefore,

$$D = 0{\cdot}26\,(1 + \alpha \times 10^{6}) \tag{4}$$

This equation permits the prediction of the dilation from the thermal expansion data. The figures so obtained are compared with the experimental results in Table 4.

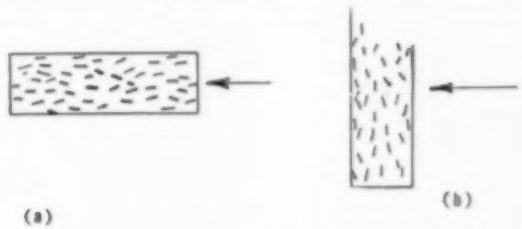

FIG. 6.—Anisotropy of polycrystalline graphite. (a) Extrusion (b) Pressing.

The model used is, of course, over-simplified especially since the possibility of expansion into the micropores, considered by some authors,[22] is ignored. Bearing this in mind, the agreement is good and the view that the increase in the average interplanar spacing is about 5 per cent is supported.

Physical appearance of the material

In appearance the sodium–graphite preparations resemble graphite closely but have a distinct violet tinge. This is consistent with the lamellar structure and low sodium content since, as is well known, the K–, Rb– and Cs–graphite lamellar

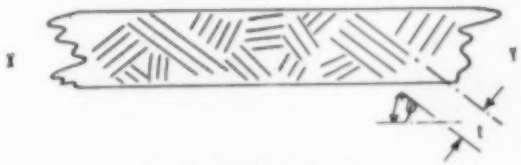

FIG. 7.—Calculation of dilation.

compounds are strongly coloured and resemble graphite more closely as the proportion of metal decreases; e.g. C_8K is bronze-copper colour[3,5] and $C_{24}K$ blue-black.[5]

DISCUSSION

The ideal formula $C_{64}Na$ is in accord with the view that only every eighth interplanar gap contains sodium since this composition would arise if the sodium within this interplanar gap is arranged very simply, for example as in Fig. 8. This arrangement was assumed in calculating Table 3. It is similar to that suggested by recent workers on potassium– and rubidium–graphite.[3,5] They believe however that,

[21] D. P. RILEY, *Proc. Phys. Soc.* **57**, 493 (1945).
[22] L. D. LOCH and A. E. AUSTIN, *Proceedings of the Conferences on Carbon* p. 65. University of Buffalo (1955).

TABLE 3.—X-RAY DIFFRACTION RESULTS

COMPARISON OF CALCULATED AND OBSERVED LINE POSITIONS AND INTENSITIES (THE STRUCTURE ASSUMED IN CALCULATIONS IS GIVEN IN FIGS. 5 AND 8)

Line index†	"Line position"*		Line intensity	
	$1/d^2$ observed	$1/d^2$ calculated	Observed**	Calculated‡
00016	0·0816	0·0815	$s+$	1000
00018	0·1030	0·1031	s	315
$20\bar{2}0$	0·2198	0·2198	m	36
$20\bar{2}7$	0·2358	0·2353	$w+$	22
$20\bar{2}9$	0·2450	0·2455	$m+$	166
$20\bar{2}11$	0·2587	0·2583	$w-$	13
00032	0·3258	0·3259	$w+$	14
00034	0·3678	0·3679	$s-$	52
$20\bar{2}25$	0·4186	0·4187	$m-$	49
$22\bar{4}0$	0·6594	0·6593	m	69
$22\bar{4}16$	0·7411	0·7407	m	56
$22\bar{4}18$	0·7625	0·7624	$w+$	29
00050	0·7953	0·7957	m	15
$40\bar{4}0$	0·8792	0·8790	vw	2
$40\bar{4}7$	0·8950	0·8946	vvw	2
$40\bar{4}9$	0·9044	0·9048	$w-$	12
$22\bar{4}32$	0·9850	0·9852	$w-$	9
$22\bar{4}34$	1·0262	1·0272	m	46
$40\bar{4}25$	1·0775	1·0779	$w-$	9
00066	1·3863	1·3864	$w+$	4
$40\bar{4}41$	1·4138	1·4140	$vw:d$	8
$22\bar{4}50$	1·4546	1·4550	$m+$	68
00068	1·4730	1·4717	$vvw:d$	6
$24\bar{6}0$	1·5382	1·5383	$w+$	5
$24\bar{6}7$	1·5541	1·5539	$w-$	5
$24\bar{6}9$	1·5634	1·5640	$m-$	28

* "Line position" = $1/d^2$ where d is the planar spacing in Å
† Only important lines listed
‡ Relative to an arbitary value of 1000 for the 00016 line
** Descending order of intensities $s+$; s; $s-$; m; $m-$; $w+$; w; $w-$; vw; vvw; d = diffuse line

TABLE 4.—DILATION IN SODIUM

Material	Thermal expansion coefficient average from −196 to 25°C	Dilation (%)	
		Calc.	Expl.
Graphite I ∥	2·7	0·96	0·92
Graphite I ⊥	1·5	0·65	0·60
Graphite II ∥	1·3	0·60	0·77
Graphite III ∥	0·6	0·41	0·36
Graphite IV ⊥	2·8	0·99	1·0
Graphite IV ∥	0·68	0·44	0·41
Graphite V	7·9	2·3	2·3

⊥ and ∥ indicate, respectively, samples cut with axes *perpendicular* to and *parallel* to extrusion direction.

with compounds poor in metal, the metal layers are more sparsely inhabited than is suggested here, one in every three of the alkali metal atoms in Fig. 8 (marked ×) being absent; this arrangement seems unlikely for the present sodium compound since it would give a composition of $C_{96}Na$.

It is interesting that, in the arrangement of the graphite sheets with respect to each other (Fig. 5), there is apparently a change from the normal graphite *A B A B*

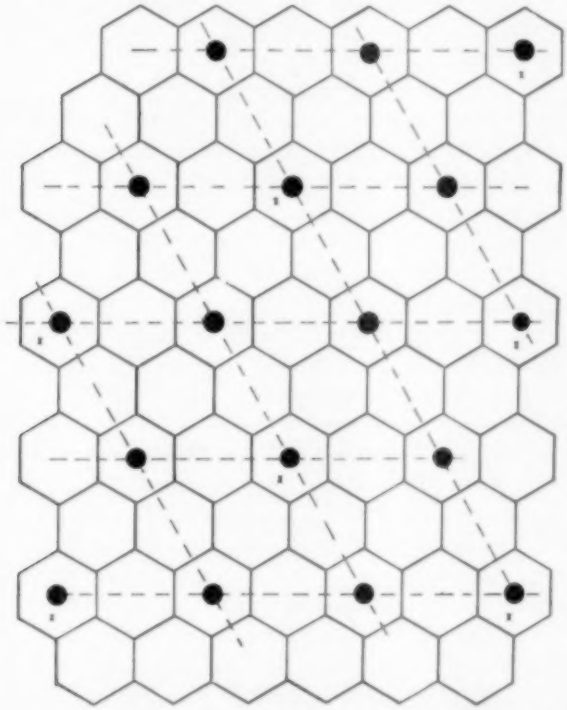

FIG. 8.—Sodium–graphite compound. Suggested arrangement of sodium in interplanar gap. (Sodium = ●)

arrangement to the arrangement *A A* (as in rhombohedral graphite) at the interplanar gap where the sodium is intercalated.

The nature of the bonds between the sodium and the graphite is not known for certain but is probably 'metallic' in character,[6,7,18,19] electrons being donated by the sodium to the π orbits of the graphite. HENNIG,[7,16,23,24] by measuring their electrical properties, concluded that in most graphite lamellar compounds about one third of the intercalated material donates electrons in this way. The bonding is in this case non-localized and the amount of sodium in the interlayer gap might be expected to be slightly variable. This may partly explain the range of stable compositions. In addition there is the possibility that the sodium layers may not always be separated by eight graphite layers but occasionally by, for example, seven or nine. On this point the X-ray results are inconclusive: they indicate that while there is a

[23] G. R. HENNIG, *J. Chem. Phys.* **20**, 1443 (1952).
[24] G. R. HENNIG and M. DZURUS, *Phys. Rev.* **98**, 227 (1955).

strong predominance of the 'spacing of eight' other spacings may occur occasionally.

The 'spacing of eight' is puzzling; it may be conjectured that mutual electrostatic repulsion of the sodium layers is involved. An alternative hypothesis is that the penetration of the sodium occurs only where there are defects in the stacking of the graphite sheets. In this case the sodium–graphite compound would bear some resemblance to the 'residual' compounds studied by HENNIG.[25] This hypothesis seems to be ruled out however, since the range of powders studied had different frequencies of stacking faults but all gave precisely the same increase in average interplanar spacing. The average frequency of stacking faults (i.e. $1/p$) was: A, every 50; B, every 30; C, every 7; D, every 2–3.

These experiments also make it improbable that some other unspecified defect is involved in binding the sodium for it is unlikely that the incidence of such a defect would be the same in all these graphites.

With potassium and rubidium, series of lamellar compounds exist with metal layers separated by one, two, three, four or five graphite layers,[2,3,4,5,26] although no other compound having the 'spacing of eight' as with sodium has yet been reported. The existence of these series prompted a search for other sodium–graphite lamellar compounds. Preparations of sodium and graphite corresponding to various compositions between $C_{90}Na$ and $C_{26}Na$ were made at various temperatures between 120°C and 500°C and using heating times between 0·25 and 6 hr.

The compound, however, was always $C_{64}Na$ irrespective of the experimental conditions or of which of the graphites, A, B, C or D, were used. It must be stressed however that other compounds may exist under other conditions. It is also possible that *non-graphitic* materials give different compounds. In this connexion it may be mentioned that X-ray diffraction patterns suggest that carbon black gives a compound richer in sodium and having Δ_c greater than 5%; previous workers[26,27,28,29] have also noted differences in the behaviour of graphites and carbons towards alkali metals. More work is necessary to clarify this.

In reporting the compound $C_{64}Na$ some account must be taken of its non-discovery by previous workers in this field.[2,3,26] This may be due to the rather low concentration of sodium in the compound. For this reason, small amounts of air or moisture rapidly convert it to graphite and a mixture of sodium compounds. Moreover, previous workers have looked for compounds containing much more sodium and the large excess of sodium used may have masked the formation of the compound.

Finally, there is the influence of small amounts of impurities, on the sodium–graphite interaction. Certain of the impurities, in particular potassium (of which there may be some 700 p.p.m. in the least pure samples), will themselves react with graphite to give lamellar compounds but not in sufficient quantities to be detectable by X-ray diffraction. More important is the possibility that impurities may promote the sodium–graphite interaction and it has been claimed that both caesium[13] and ammonia[18] have this effect. In these cases the amounts of "impurity" used were comparable to the amount of sodium but HENNIG also

[25] G. R. HENNIG, *J. Chem. Phys.* **20**, 1438 (1952).
[26] G. L. MONTET, AECU-3142 (1952). Declassified (1956).
[27] H. L. RILEY, *Fuel Sci. Practice* **24**, 1 (1945).
[28] G. TAMMANN and A. SWORYKIN, *Z. Anorg. Chem.* **168**, 218 (1927).
[29] N. PLATZER, *C. R. Acad. Sci., Paris* **245**, 1925 (1957).

believes[7,18,30] that mere traces are effective and considers[31] that the amount of potassium in the materials of the present work may be sufficient. However a subsidiary experiment with the purest sodium readily available (50 p.p.m. potassium) gave the same sodium–graphite compound as did the less pure specimens of sodium (usually 100–130 p.p.m. potassium, but 700 p.p.m. for the susceptibility measurements). It would be interesting, though experimentally difficult, to study even purer sodium.

Acknowledgements—Thanks are due to several colleagues at A.E.R.E., and in particular Mr. S. WILSON for the X-ray diffraction work and the interpretation of the results, Mr. A. D. LECLAIRE for the magnetic susceptibility determinations and Messrs. M. MORETON-SMITH and G. HALL for much of the experimental work.

[30] B. SMALLER, G. R. HENNIG and E. L. YASAITIS, *Phys. Rev.* **97**, 239 (1955).
[31] G. R. HENNIG. Private communication (1957).

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ORGANOMETALLIC COMPLEXES—IV[1]

ÜBER DIE REAKTION VON SUBSTITUIERTEN ACETYLENVERBINDUNGEN MIT EISENTETRACARBONYL

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Abstract—The reaction of iron dodecacarbonyl with substituted acetylenes yields a number of new kinds of organometallic complexes. This is illustrated by the example of phenylacetylene and diphenylacetylene; the types of compounds obtained are described and their structures discussed. The acetylenic components are transformed stereospecifically, in a single-stage reaction, into organic double-bond systems, which contain occasionally keto-groups as well and which represent the organic ligands of these π-complexes. This leads to new possibilities for the synthesis of organic compounds from alkynes and metal carbonyls.

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In einer einführenden Abhandlung[2] wurde bereits auf die Reaktion von Eisentetracarbonyl, $[Fe(CO)_4]_3$, mit Alkinen hingewiesen. Sie führte zur Entdeckung einer Reihe neuer Organoeisencarbonyl-Verbindungen.

Erhitzt man Eisentetracarbonyl in einem inerten Lösungsmittel, so wird es zu Eisenpentacarbonyl, Kohlenoxyd und eisenhaltigen Niederschlägen zersetzt. In Gegenwart von Acetylenverbindungen dagegen werden verschiedene Typen metallorganischer Eisencarbonylkomplexe gebildet, deren Anzahl von den Substituenten des eingesetzten Acetylens abhängt. Diese Umsetzung wurde mit den verschiedensten Alkinen ausgeführt; die zahlreichsten Verbindungstypen entstanden dabei mit Phenylacetylen und Diphenylacetylen (Tolan), sowie mit deren Halogensubstitutionsprodukten. Lediglich mit Bis-trimethylsilyl-acetylen, *p,p'*-Dinitrotolan und Acetylendicarbonsäure konnten bisher keine entsprechenden Komplexverbindungen erhalten werden. Manche Komplextypen entstehen nur mit mono-, andere ausschliesslich mit disubstituierten Acetylenen.

In der vorliegenden Abhandlung soll daher diese allgemeine Reaktion des Eisentetracarbonyls am Beispiel von Tolan und Phenylacetylen eingehend beschrieben werden.

Die so darstellbaren Organoeisencarbonyl-Verbindungen sind kristalline, an der Luft stabile π-Komplexe.[2] Sie sind in organischen Lösungsmitteln meist gut löslich. Nur wenige Verbindungen zeigen einen scharfen Schmelzpunkt, im allgemeinen schmelzen sie unter Zersetzung. Bei allen Komplexen fehlt im IR-Spektrum die Absorption der Acetylendreifachbindung. Charakteristisch für die einzelnen Komplextypen sind dagegen Anzahl und Anordnung der Valenzschwingungen der Kohlenoxydliganden im Bereich von 5 μ. Einige der Verbindungen zeigen darüber hinaus im Bereich von 6·0–6·2 μ eine intensive Bande, die der Absorption einer Carbonylgruppe des organischen Liganden zuzuordnen ist.

[1] III. Mitteil.: D. A. BROWN, *J. Inorg Nucl. Chem.* **10**, 49 (1959).
[2] I. Mitteil.: W. HÜBEL, E. H. BRAYE, A. CLAUSS, E. WEISS, U. KRÜERKE, D. A. BROWN, G. S. D. KING u. C. HOOGZAND, *J. Inorg. Nucl. Chem.* **9**, 204 (1959).

DIE REAKTION VON EISENTETRACARBONYL MIT TOLAN

Erhitzt man Eisentetracarbonyl in einem inerten Lösungsmittel (vorzugsweise Petroläther) mit Tolan auf 80–90° C, so nimmt die anfangs tiefgrüne Reaktionslösung langsam eine dunkelbraune Färbung an. Gleichzeitig werden $Fe(CO)_5$ und Kohlenoxyd gebildet. Die Lösung enhält sechs verschiedene Komplexverbindungen (Tabelle 1), die sich chromatographisch leicht trennen lassen. Daneben findet man kleinere Mengen organischer Reaktionsprodukte wie Hexaphenylbenzol, entstanden

TABELLE 1.—BRUTTOFORMELN UND PHYSIKALISCHE EIGENSCHAFTEN DER "EISENCARBONYL-TOLAN-KOMPLEXE"

Summenformel	Farbe	Dichte (g/cc)	Schmelzpunkt (°C)	Kristallsystem	IR-aktive CO-Valenzschwingungen[c]	
					im 5-μ-Gebiet	im 6-μ-Gebiet
$Fe(CO)_3(C_6H_5C_2C_6H_5)_1$	hellgelb	1·39	234[a]	monoklin	4·92 5·09 5·18	—
$Fe(CO)_4(C_6H_5C_2C_6H_5)_1$	gelb	1·35	ca. 180[b]	triklin	4·85 4·97 5·03	6·09
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)$	rot	1·67	150[a]	triklin	4·85 4·94 5·05 5·20	—
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$	orange	1·44	ca. 200[b]	monoklin	4·82 4·94 5·02 5·06 5·19	—
$Fe_2(CO)_7(C_6H_5C_2C_6H_4)_2$	rot	1·53	ca. 160[b]	monoklin	4·82 4·87 4·96	6·00
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$	schwarz	1·57	ca. 210[b]	monoklin	4·84 4·97 5·06 5·40[d]	—

Bermerkungen:
(*a*) schmilzt scharf; (*b*) schmilzt unter Zersetzung; (*c*) die Substanzen wurden in KBr vermessen; (*d*) ist der Dehnfrequenz von Brückenkohlenoxyd zuzuordnen.

durch die Trimerisierung von Tolan, sowie Tetraphenylcyclopentadienon (Tetracyclon), das bei der Zersetzung einiger Komplexe gebildet wird.

Wie man aus Tabelle 1 ersieht, entstehen bei der Umsetzung von Eisentetracarbonyl mit Tolan neben einkernigen Komplextypen auch Verbindungen, die zwei, bzw. drei Eisenatome im Molekül aufweisen. Im Gegensatz zu den Reaktionsprodukten aus Phenylacetylen werden maximal nur zwei Diphenylacetylene in die Komplexverbindungen eingebaut. Sämtliche nachstehend beschriebenen "Eisencarbonyl-Tolan-Komplexe" sind diamagnetisch. Sie lösen sich leicht in Benzol und Aceton, weniger in Petroläther und Alkoholen.

Einkernige Komplextypen

1. $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$. Dieser hellgelbe Komplex entsteht bei der Umsetzung von Eisentetracarbonyl mit Tolan nur in sehr geringen Mengen; er lässt sich besser durch die Reaktion von $Fe(CO)_5$ mit Diphenylacetylen bei höheren Temperaturen darstellen.[2] Die Verbindung ist thermisch ausserordentlich stabil, schmilzt scharf bei 234°C und kann ab 180°C im Vakuum sublimiert werden.

$Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ wird selbst bei längerem Erhitzen mit Kohlenoxyd unter Druck nicht verändert. Beim reduktiven Abbau mit $LiAlH_4$ erhält man 1:2:3:4-Tetraphenylbutadien in hohen Ausbeuten; Natrium in flüssigem Ammoniak ergibt fast ausschliesslich das bei 96°C schmelzende 1:2:3:4-Tetraphenylbutan, neben wenig der bei 185°C schmelzenden stereoisomeren Form. Doppelbindungen im organischen Liganden der Komplexverbindung konnten durch Epoxydation mit Peressigsäure nicht nachgewiesen werden; die Verbindung wurde selbst unter scharfen Reaktionsbedingungen nicht verändert.

Diese Abbau-Versuche zeigen, dass die beiden Tolanmoleküle im Komplex jedenfalls zu einem Dien-System verbunden sind.[3] Dadurch können für den Komplextyp $Fe(CO)_3(RC_2R')_2$ zwei Strukturen vorgeschlagen werden. In Fig. 1 füllen die vier π-Elektronen eines Cyclobutadienrings zusammen mit den 6 Valenzelektronen der 3 Kohlenoxydliganden die Elektronenschale des Zentralatoms zur Edelgaskonfiguration auf. Auf diese Möglichkeit einer Stabilisierung des unbekannten

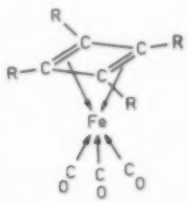

FIG. 1.

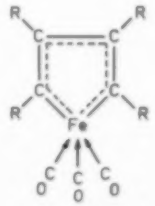

FIG. 2.

Cyclobutadiensystems durch Komplexbildung wurde bereits in mehreren theoretischen Arbeiten[4,5] hingewiesen. Die experimentell gefundenen, kettenförmigen Abbauprodukte schliessen diesen Strukturvorschlag nicht aus; es erscheint durchaus möglich, dass der unbekannte Vierring aufspaltet, bevor er durch Hydrierung

[2] Aus Arbeiten von L. I. SMITH u. H. H. HOEHN, (*J. Amer. Chem. Soc.* **63**, 1184 (1941)) ist bekannt, dass Tolan unter Einwirkung von Natrium in inerten Lösungsmitteln Tetraphenylbutadien bildet. Mit Natrium in flüssigem Ammoniak entsteht nach eigenen Versuchen nur Dibenzyl.

[4] H. C. LONGUET-HIGGINS u. L. E. ORGEL, *J. Chem. Soc.* 1969 (1956).

[5] II. Mitteil.: D. A. BROWN, *J. Inorg. Nucl. Chem.* **10**, 39 (1959).

stabilisiert wird. Bei einem anderen Strukturvorschlag (Fig. 2) bildet das zugrundeliegende Diensystem durch σ-Bindungen mit dem Eisenatom einen Fünfring. Von den vier nicht lokalisierten π-Elektronen des organischen Liganden werden zwei noch zusätzlich am Zentralatom anteilig, wie es in Fig. 2 schematisch angedeutet ist.

2. $Fe(CO)_4(C_6H_5C_2C_6H_5)_2$. Von dieser Verbindung ist in Tabelle 1 die trikline Form angeführt, die sich aus Benzol-Methanol bildet. Aus Benzol-Petroläther erhält man eine andere Kristallform, die sich bei 130–140°C in die oben genannte Modifikation umwandelt.

Der Komplex sublimiert im Vakuum ab 140°C, wobei er sich teilweise zu Tetracyclon zersetzt. Dieses entsteht auch beim Schmelzen in hohen Ausbeuten. Die Struktur der Komplexverbindungals Tetracyclon-eisentricarbonyl (Fig. 3) der Formel (Tetracyclon)$Fe(CO)_3$ konnte durch die direkte Synthese aus Eisencarbonylen und Tetracyclon bewiesen werden.[2]* Die intensive Bande im IR-Spektrum bei 6·09 μ ist der Absorption der Ketogruppe des komplexgebundenen Tetracyclons zuzuordnen.

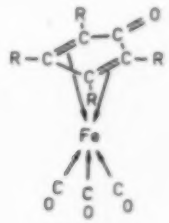

FIG. 3.

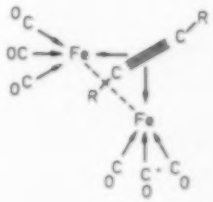

FIG 4.

Zweikernige Komplextypen

1. $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$. Diese rote Komplexverbindung entsteht bei der Reaktion von Eisentetracarbonyl mit Tolan nur in kleinen Mengen. Sie kann ab 100°C im Vakuum sublimiert werden. Die Feinstruktur der Röntgen-K-Absorptionskante zeigt einen auffallend ähnlichen Kurvenverlauf wie bei $[Co(CO)_4]_2$[6] mit einem schwachen Vormaximum bei 4·5 eV und einem Maximum bei 17 eV. Der reduktive Abbau der Verbindung mit Natrium in flüssigem NH_3 ergibt Dibenzyl in hohen Ausbeuten.

Der Komplex entspricht rein formal den schon früher beschriebenen Kobaltverbindungen der Formel $Co_2(CO)_6(RC_2R')$.[7] Nach den bisherigen Ergebnissen wird eine Struktur nach Fig. 4 vorgeschlagen, wobei die beiden π-Elektronenpaare der Kohlenstoffdreifachbindung an den Eisenatomen anteilig werden. Im Hinblick auf die thermische Stabilität der diamagnetischen Verbindung liegt es nahe, Eisen-Eisen-Bindungen anzunehmen.

2. $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$. Dieser Komplextyp entsteht als Hauptprodukt bei der Reaktion von $[Fe(CO)_4]_3$ mit Tolan und ist auch durch die Umsetzung von Tolan mit anderen Eisencarbonylen leicht zugänglich.[2]

Die orangegelbe Verbindung kann ab 130°C im Vakuum sublimiert werden.

* Über diese und ähnliche Umsetzungen auch mit anderen Metallcarbonylen wird demnächst gesondert berichtet.

[6] K. BÖCKE, *Z. Phys. Chem.* **10**, 60 (1957).

[7] H. W. STERNBERG, H. GREENFIELD, R. A. FRIEDEL, J. H. WOTIZ, R. MARKBY u. I. WENDER, *J. Amer. Chem. Soc.* **76**, 1457 (1954); H. GREENFIELD, H. W. STERNBERG, R. A. FRIEDEL, J. H. WOTIZ, R. MARKBY u. I. WENDER, *J. Amer. Chem. Soc.* **78**, 120 (1956).

Magnetische Messungen ergeben für den Komplex Diamagnetismus entsprechend einer extrapolierten Molsuszeptibilität $\chi_{mol}^{\infty\,°K} = (-260 \pm 15) \times 10^{-6}$ cm³/Mol. Die Feinstruktur der Röntgen-*K*-Absorptionskante ist praktisch die gleiche wie bei $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$.

Für den Komplextyp $Fe_2(CO)_6(RC_2R')_2$ können mehrere Strukturen diskutiert werden. Bei einer Struktur nach Fig. 5 werden die beiden Acetylenliganden mit

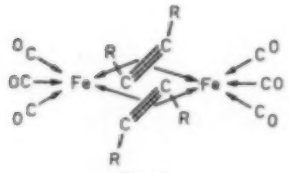

FIG. 5.

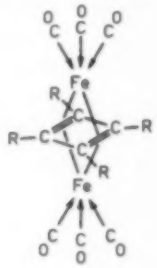

FIG. 6.

ihren π-Elektronenpaaren an jedem Eisenatom anteilig und füllen dessen Elektronenschale zur Edelgaskonfiguration auf. Die Acetylenkomponenten wären also in ähnlicher Weise gebunden wie es für den Komplex $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$ (Fig. 4) vorgeschlagen wurde. Ein zweiter Strukturvorschlag nach Fig. 6, worin das unbekannte Cyclobutadiensystem durch Komplexbildung stabilisiert ist, wäre nach theoretischen Betrachtungen von BROWN[5] möglich. Bei einer Struktur nach Fig. 7 dagegen bilden die beiden Alkine ein Butadiensystem, das mit dem Eisenatom einer $Fe(CO)_3$-Gruppe als Heteroatom einen Fünfring ergibt. Die zweite $Fe(CO)_3$-Gruppe wird senkrecht zur Ebene des Fünfrings durch die π-Elektronen des Butadiensystems gebunden. Eine koordinative Kovalenz zwischen den beiden Eisenatomen wird dem experimentell gefundenen Diamagnetismus und der Stabilität des Komplexes gerecht.

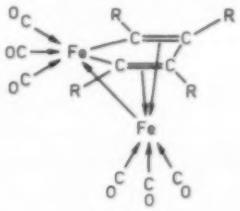

FIG. 7.

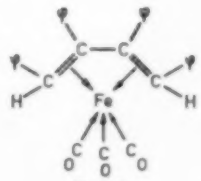

FIG. 8.

Die Existenz einer Struktur nach Fig. 7 konnte kürzlich durch röntgenographische Arbeiten von HOCK u. MILLS[8] für einen Komplex der Summenformel $Fe_2C_{12}H_8O_8$[9] bewiesen werden.

Im Hinblick auf das vorliegende Strukturproblem wurden verschiedene Abbaureaktionen ausgeführt. Bei der Oxydation von $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ mit Brom in Eisessig entsteht hauptsächlich Tetracyclon-eisentricarbonyl (Fig. 3) neben wenig Tetracyclon. Eine Lösung der Komplexverbindung wird durch Belichten zu Tetracyclon und Tetraphenylbutadien-eisentricarbonyl (Fig. 8) abgebaut. In Gegenwart

[8] A. A. HOCK u. O. S. MILLS, *Proc. Chem. Soc.* 233 (1958).
[9] R. CLARKSON, E. R. H. JONES, P. C. WAILES u. M. C. WHITING, *J. Amer. Chem. Soc.* **78**, 6206 (1956). Vgl. ferner W. REPPE u. H. VETTER, *Annalen* **582**, 133 (1953) und H. W. STERNBERG, R. A. FRIEDEL, R. MARKBY u. I. WENDER, *J. Amer. Chem. Soc.* **78**, 3621 (1956).

von Schwefel ergibt die Photolyse von $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ in Lösung ausschliesslich Tetraphenylthiophen als organisches Reaktionsprodukt. Beim Erhitzen mit Kohlenoxyd unter Druck bildet sich $Fe(CO)_5$ und Tetracyclon-eisentricarbonyl (Fig. 3).

Versuche zur katalytischen Hydrierung der Komplexverbindung mit Wasserstoff an Platin oder Raney-Nickel waren ohne Erfolg. Dagegen wird $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ mit $LiAlH_4$ in kurzer Zeit vollständig zu einem Gemisch von 1:2:3:4-Tetraphenylbuten-1 und dem hochschmelzenden 1:2:3:4-Tetraphenylbutan abgebaut, das gelegentlich noch etwas 1:2:3:4-Tetraphenylbutadien enthält. Ähnliche Reaktionsprodukte entstehen auch mit Natrium in flüssigem Ammoniak. Bei diesen Reaktionen konnte als Zwischenprodukt auch 1:2:3:4-Tetraphenylbutadien-eisentricarbonyl (Fig. 8) isoliert werden. Seine Struktur als Dien-Komplex ergab sich durch die Synthese aus $Fe(CO)_5$ und 1:2:3:4-Tetraphenylbutadien.[10] Diese Komplexverbindung entsteht auch in guten Ausbeuten, wenn man starke Basen wie Natriumamid oder Natriumalkoholat auf $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ einwirken lässt.

Aus diesen Abbaureaktionen geht hervor, dass im Komplex $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ die beiden Tolanmoleküle zu einem Butadiensystem verbunden sein müssen, was eine Struktur nach Fig. 5 ausschliesst.[3] Da die Verbindung ein grosses Dipolmoment ($3{\cdot}3 \pm 0{\cdot}2$ D in Benzol) besitzt, scheidet allgemein eine zentrosymmetrische Struktur wie in Fig. 5 und Fig. 6 aus. Der Strukturvorschlag in Fig. 7 erscheint am besten geeignet, die beschriebenen Umsetzungen zu erklären. Der Austausch einer $Fe(CO)_3$-Gruppe gegen Kohlenoxyd unter Bildung von (Tetracyclon)$Fe(CO)_3$, bzw. Tetracyclon wird damit verständlich, ebenso die Entstehung des Dien-Komplexes (Tetraphenylbutadien)$Fe(CO)_3$ unter Aufnahme von zwei Wasserstoffatomen. Auch die Bildung von Thiophenderivaten bei der Einwirkung von Schwefel ergibt sich aus Fig. 7. Diese Abbauprodukte zeigen, dass die beiden Eisenatome im Komplex verschieden stark gebunden sind, wobei die Bindungen zur $Fe(CO)_3$-Gruppe im Ring, die hauptsächlich σ-Charakter besitzen dürften, erwartungsgemäss schwächer sind.

3. $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$. Dieser tiefrote Komplex entsteht bei der Reaktion von Eisentetracarbonyl mit Tolan in geringen Mengen; bessere Ausbeuten erhält man bei Verwendung von Dieisenenneacarbonyl.[2] Aus Benzol-Petroläther erhält man diese Verbindung in monoklinen, roten Kristallen mit 1/2 Mol Kristallbenzol; sie schmelzen bei etwa 160°C unter Zersetzung.

$Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2 \cdot 1/2\ C_6H_6$ ist diamagnetisch, entsprechend der extrapolierten Molsuszeptibilität $\chi_{mol}^{\infty\,°K} = (-245 \pm 15) \times 10^{-6}$ cm³/Mol. Auch hier zeigt die Feinstruktur der Röntgen-K-Absorptionskante einen Kurvenverlauf, der mit dem der Komplexverbindung $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$ und $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ nahezu übereinstimmt.

Für den Komplextyp $Fe_2(CO)_7(RC_2R')_2$ können wiederum mehrere Strukturen diskutiert werden. Theoretische Überlegungen von BROWN[1] haben ergeben, dass eine Struktur nach Fig. 9 stabil sein müsste; hier sind beide $Fe(CO)_3$-Gruppen senkrecht zur Ringebene des Cyclopentadienons angeordnet.

Andererseits ist in Anlehnung an den Komplextyp $Fe_2(CO)_6(RC_2R')_2$ (Fig. 7) auch eine Struktur nach Fig. 10 in Betracht zu ziehen. Dabei bildet das Eisenatom einer $Fe(CO)_3$-Gruppe zusammen mit 2 Tolanmolekülen und Kohlenoxyd einen Sechsring, während die zweite $Fe(CO)_3$-Gruppe senkrecht zur Ringebene durch die π-Elektronen

[10] Vergl. B. F. HALLAM u. P. L. PAUSON, *J. Chem. Soc.* 642 (1958).

des Dienonsystems gebunden wird. Eine koordinative Kovalenz zwischen beiden Metallatomen wird dem experimentell gefundenen Diamagnetismus gerecht. Im IR-Spektrum wird die scharfe Bande bei 6·00 μ der Absorption der Ketogruppe dieses komplexgebundenen Dienonsystems zugeordnet.

Die thermische Zersetzung von $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ in Lösung oder die Photolyse ergeben (Tetracyclon)$Fe(CO)_3$ und Tetracyclon, was aus jedem der beiden Strukturvorschläge zu erwarten wäre. Auch beim Erhitzen mit Kohlenoxyd unter Druck entsteht neben Pentacarbonyl hauptsächlich der Komplex (Tetracyclon)-$Fe(CO)_3$. Dagegen erhält man beim reduktiven Abbau mit $LiAlH_4$ oder mit Natrium

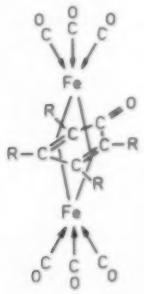

FIG. 9.

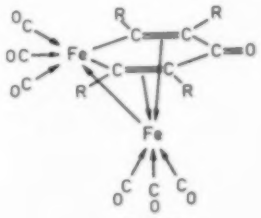

FIG. 10.

in flüssigem Ammoniak neben Cyclopentadienonderivaten auch Tetraphenylchinon, bzw. -hydrochinon. Die Bildung eines Chinons unter diesen milden Reaktionsbedingungen lässt sich nur aus der Struktur nach Fig. 10 erklären.

Die beschriebenen Versuche zeigen auch, dass bei der Zerstörung des Komplexes der Ringschluss zum Fünfring leichter erfolgt als der Eintritt von Kohlenoxyd unter Bildung des Chinonderivates.

Dreikernige Komplextypen

$Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$. Verbindungen von diesem Typ konnten bisher nur bei Umsetzungen mit Eisentetracarbonyl erhalten werden. Bei der Reaktion mit Tolan entsteht die schwarze Verbindung $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ in guten Ausbeuten.

Nach dieser Summenformel wäre es naheliegend, diese Komplexverbindung als ein Eisentetracarbonyl aufzufassen, bei welchem ein Teil der Kohlenoxydliganden durch Diphenylacetylen substituiert ist. Diese Vorstellung trifft jedoch nicht zu, worauf schon die Entstehung des gelben Komplexes $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ beim Erhitzen der Verbindung auf 150°C hinweist. Die Verbindung $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ spaltet bevorzugt Eisen und Kohlenoxyd ab, was z.B. bei Substitutionsversuchen mit Triphenylphosphin besonders deutlich wird. Hierbei lassen sich die Reaktionsbedingungen so wählen, dass neben $Fe(CO)_3[P(C_6H_5)_3]_2$ praktisch nur $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ entsteht.*

Mit $LiAlH_4$ wird bei Zimmertemperatur nur ein Teil des $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ zu 1:2:3:4-Tetraphenylbutan und dem Dien-Komplex (Tetraphenylbutadien)$Fe(CO)_3$ abgebaut. Bei höherer Temperatur verläuft der Abbau vollständig; es entsteht

* Über die Substitutionsreaktionen der hier beschriebenen Komplexverbindungen wird demnächst berichtet.

hauptsächlich 1:2:3:4-Tetraphenylbutan (F.P. 185°C) neben wenig 1:2:3:4-Tetraphenylbuten-1. Die gleichen Reaktionsprodukte wurden auch bei der Umsetzung mit Natrium in flüssigem NH_3 erhalten.

Diese experimentellen Ergebnisse lassen den Schluss zu, dass in $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ die beiden Tolanmoleküle ebenfalls als ein Butadiensystem vorliegen und damit die Struktur des Komplexes $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ (Fig. 7) bereits vorgebildet ist. Der zusätzliche Einbau von einem Eisenatom und zwei Kohlenoxydliganden muss nach dem IR-Spektrum unter Ausbildung von Kohlenoxydbrücken erfolgen.

Es soll noch darauf hingewiesen werden, dass eine violette Verbindung der gleichen Bruttoformel $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ isoliert werden kann, wenn man $[Fe(CO)_4]_3$ und Tolan nur kurz in Methanol erhitzt. Diese in CH_3OH unlöslichen, monoklinen Kristalle schmelzen bei etwa 160°C unter Zersetzung und werden in siedendem Benzol in den stabileren schwarzen Komplex $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ umgelagert. Nach ihrem IR-Spektrum besitzt die violette Verbindung keine Brückenkohlenoxydliganden. Über Komplexverbindungen, die aus Eisentetracarbonyl und Tolan in Alkoholen als Lösungsmittel entstehen, wird in einer späteren Mitteilung berichtet.

DIE REAKTION VON EISENTETRACARBONYL MIT PHENYLACETYLEN

Phenylacetylen reagiert schon ab 50°C mit Eisentetracarbonyl. Die Umsetzung wird gewöhnlich in einem inerten Lösungsmittel (vorzugsweise Petroläther und Benzol) ausgeführt und verläuft schneller als mit Tolan. Aus der Reaktionslösung lassen sich bis zu sieben verschiedene Komplexverbindungen (Tabelle 2) durch fraktionierte Kristallisation und Chromatographie isolieren. Auch hier entstehen als Nebenprodukte organische Verbindungen, die, ausser dem durch Trimerisierung von Phenylacetylen gebildeten 1:2:4-Triphenylbenzol, noch nicht näher untersucht wurden.

Man kann die Reaktion von Eisentetracarbonyl mit Phenylacetylen auch ohne Lösungsmittel ausführen. Unter solchen Reaktionsbedingungen wird als Hauptprodukt $Fe(CO)_4(C_6H_5C_2H)_5$ gebildet.

In Tabelle 2 sind die aus Phenylacetylen und Eisentetracarbonyl erhaltenen Komplexverbindungen zusammengestellt. Ein Vergleich mit den Reaktionsprodukten aus Tolan zeigt, dass hier einkernige Komplextypen bevorzugt gebildet werden und eine Verbindung mit drei Eisenatomen im Molekül überhaupt fehlt. Dagegen treten neue Typen auf, bei denen das Verhältnis der Phenylacetylen-Komponente zu Eisen besonders gross ist. Die noch nicht näher untersuchten Komplexverbindungen sollen hier lediglich kurz beschrieben werden.

Einkernige Komplextypen

1. $Fe(CO)_4(C_6H_5C_2H)_2$. Diese Substanz ist identisch mit der von JONES, WAILES u. WHITING[11] erstmals als "Eisentetracarbonyl-phenylacetylid" beschriebenen Verbindung. Sie krlstallisiert in langen, gelben Nadeln und kann ab 130°C im Vakuum sublimiert werden. In organischen Lösungsmitteln wie Benzol oder Aceton ist die Verbindung gut löslich, weniger in Petroläther und Methanol. Das IR-Spektrum zeigt, wie der entsprechende "Tolankomplex", neben den drei

[11] E. R. H. JONES, P. C. WAILES u. M. C. WHITING, *J. Chem. Soc.* 4021 (1955).

TABELLE 2.—BRUTTOFORMELN UND PHYSIKALISCHE EIGENSCHAFTEN DER "EISENCARBONYL-PHENYLACETYLEN-KOMPLEXE"

Summenformel	Farbe	Zers. Temp. (°C)	IR-aktive CO-Valenzschwingungen in KBr	
			im 5-μ-Gebiet	im 6-μ-Gebiet
$Fe(CO)_4(C_6H_5C_2H)_2$	gelb	ca. 230	4·85 4·99 5·03	6·19
$Fe(CO)_4(C_6H_5C_2H)_3$	rot-orange	ca. 156–158	4·85 5·00	6·16
$Fe(CO)_4(C_6H_5C_2H)_3$	rot	ca. 148–150 bzw. ca. 162–165	4·85 5·01	6·14
$Fe(CO)_3(C_6H_5C_2H)_4$	violett	ca. 230	4·96	5·91 6·13
$Fe(CO)_4(C_6H_5C_2H)_5$	orange	ca. 240–250	4·96 5·10	5·88 6·04
$Fe_2(CO)_6(C_6H_5C_2H)_3$	gelb-orange	ca. 180	4·82 4·90 5·00 5·13 5·20	—
$Fe_2(CO)_6(C_6H_5C_2H)_3$	schwarz	ca. 170	4·82 4·97 5·10	6·00

scharfen Absorptionsbanden für metallgebundene Kohlenoxydliganden eine intensive Bande bei 6·19 μ, die der Absorption einer Ketogruppe des organischen Liganden zuzuorden ist. Demnach ist diese diamagnetische Komplexverbindung ein Diphenyl-cyclopentadienon-eisentricarbonyl (Fig. 3). Nach der Stellung der beiden Phenyl-gruppen am Ring wären drei Isomere zu erwarten. Tatsächlich wird jedoch nur eine Verbindung gebildet. Dies zeigt, dass der Aufbau des Ringketons im Komplex in ganz spezifischer Weise erfolgt. Der Nachweis des zugrundeliegenden Cyclo-pentadienonsystems durch thermische Zersetzung ist hier schwierig, da diphenyl-substituierte Cyclopentadienone unter Dimerisierung weitere Folgeprodukte ergeben.[12]

[12] C. F. H. ALLEN. *Chem. Rev.* **37**, 232–236 (1945).

Es gelingt jedoch, den bei der thermischen Zersetzung primär abgespaltenen Cyclopentadienonring unmittelbar mit Diphenylacetylen im Sinne einer Diels-Alder-Reaktion zu 1:2:3:4-Tetraphenylbenzol umzusetzen. Daraus ergibt sich, dass im Komplex die beiden Phenylgruppen in 2:5-Stellung am Cyclopentadienonring angeordnet sind.

Wie bei der Synthese der α-Phenylacrylsäure und ihrer Ester aus Phenylacetylen[13] erfolgt auch hier die Anlagerung von Kohlenoxyd an Alkine ausschliesslich an demjenigen Kohlenstoffatom der Dreifachbindung, das die Phenylgruppe trägt. Aus weiteren Beispielen dieses Komplextypes (Fig. 3), sowie Verbindungen der Formel $Fe_2(CO)_7(RC_2R')_2$ (Fig. 10) kann allgemein gefolgert werden, dass der Eintritt der Kohlenoxydgruppe stets bei dem Kohlenstoffatom erfolgt, dessen Substituent den grösseren negativen mesomeren Effekt zeigt.

(2:5-Diphenyl-cyclopentadienon)$Fe(CO)_3$ bleibt bei allen Versuchen zum chemischen Nachweis der Ketogruppe, wie die Überführung in ein Phenylhydrazon, bzw. Oxim oder bei der Reduktion mit $NaBH_4$, unter den üblichen Reaktionsbedingungen unangegriffen. Daraus und aus der ungewöhnlichen Lage der C-O-Dehnfrequenz im IR-Spektrum (6·19 μ) wird gefolgert, dass die Ketogruppe des komplexgebundenen 2:5-Diphenyl-cyclopentadienons weitgehend polarisiert ist.

2. $Fe(CO)_4(C_6H_5C_2H)_3$. Aus der Reaktionslösung können eine orangerote und eine dunkelrote Verbindung der Summenformel $Fe(CO)_4(C_6H_5C_2H)_3$ isoliert werden, die sich in ihren physikalischen Eigenschaften deutlich unterscheiden. Beide Komplexe sind diamagnetisch und lösen sich gut in Benzol oder Aceton, weniger in Petroläther und Alkoholen. Ihre IR-Spektren stimmen in Lage und Intensität der Carbonyldehnfrequenzen überein, zeigen aber wesentliche Unterschiede im Gebiet von 6·2–15 μ. Die dunkelrote Verbindung tritt nach röntgenographischen Untersuchungen in zwei Kristallformen auf.

Beide Verbindungen der Summenformel $Fe(CO)_4(C_6H_5C_2H)_3$ ergeben beim Schmelzen ausschliesslich 1:3:5-Triphenylbenzol. Zur Struktur dieser beiden Komplexe kann erst nach Abschluss weiterer Untersuchungen Stellung genommen werden.

3. $Fe(CO)_3(C_6H_5C_2H)_4$. Diese rot-violette Verbindung wurde lediglich bei den Umsetzungen von $[Fe(CO)_4]_3$ mit Phenylacetylen ohne Lösungsmittel in kleinen Mengen erhalten. Sie ist in organischen Lösungsmitteln sehr wenig löslich. Das IR-Spektrum zeigt nur *eine* Absorptionsbande für die Valenzschwingung metallgebundener Kohlenoxydgruppen.

4. $Fe(CO)_4(C_6H_5C_2H)_5$. Der in orangefarbenen Nadeln kristallisierende Komplex entsteht in guten Ausbeuten, wenn man $[Fe(CO)_4]_3$ in Phenylacetylen auf 60–75°C erhitzt. Die Verbindung löst sich gut in Tetrahydrofuran, weniger in Benzol, Aceton und Äther und ist in Alkoholen, sowie in Petroläther praktisch unlöslich. Sie ist thermisch ausserordentlich stabil und schmilzt erst bei 240–250°C unter Zersetzung. Über ihre Struktur mit der ungewöhnlichen Summenformel $Fe(CO)_4(C_6H_5C_2H)_5$ wird nach Abschluss weiterer Versuche berichtet.

Zweikernige Komplextypen

1. $Fe_2(CO)_6(C_6H_5C_2H)_2$. Diese orangegelbe Verbindung sublimiert ab 100°C im Vakuum und ist in den gebräuchlichen organischen Lösungsmitteln sehr leicht löslich.

[13] W. Reppe, *Annalen* **582**, 5 (1953); E. R. H. Jones, T. Y. Shen u. M. C. Whiting, *J. Chem. Soc.* 766 (1951).

Das IR-Spektrum zeigt eine Bandengruppe für metallgebundene Kohlenoxydliganden, wie sie für den Komplextyp $Fe_2(CO)_6(RC_2R')_2$ charakteristisch ist. Es wird eine Struktur nach Fig. 7 angenommen, die bei dem entsprechenden "Tolankomplex" ausführlich diskutiert wurde.

Bei $Fe_2(CO)_6(C_6H_5C_2H)_2$ wurde ebenfalls von den drei möglichen isomeren Diphenylbutadienliganden immer nur eine Komplexform erhalten, was wiederum auf die stereospezifische Bildung dieser Komplexverbindungen hinweist.

2. $Fe_2(CO)_6(C_6H_5C_2H)_3$. Der in schwarzen, monoklinen Prismen kristallisierende diamagnetische Komplex ist in organischen Lösungsmitteln schwer löslich. In siedendem Benzol wird der Komplex zu den beiden beschriebenden Verbindungen der Summenformel $Fe(CO)_4(C_6H_5C_2H)_3$ abgebaut. Man darf daher bei seiner Darstellung eine Reaktionstemperatur von 70°C nicht überschreiten. Es ist bemerkenswert, dass diese Verbindung bei den Umsetzungen ohne Lösungsmittel nie beobachtet wurde.

Erhitzt man die Substanz zum Schmelzen, so entsteht 1:3:5-Triphenylbenzol in hohen Ausbeuten. Inwieweit der Benzolring in der Struktur des Komplexes bereits vorgebildet ist, kann erst nach Abschluss weiterer Versuche diskutiert werden.

BESCHREIBUNG DER VERSUCHE

(Mitbearbeitet von I. Caplier und R. Vannieuwenhoven)*

1. *Die Umsetzung von Eisentetracarbonyl mit Tolan*

25 g Eisentetracarbonyl[14] (0·05 Mol) und 25 g Tolan (0·14 Mol) werden in 2·5 L Petroläther (Kp. 85–90°C) am Rückfluss erhitzt bis die tiefgrüne Farbe der Lösung nach 1·5–2 Stunden praktisch verschwindet. Aus der filtrierten Reaktionslösung lassen sich die gebildeten Komplexverbindungen am besten chromatographisch mit saurem oder neutralem Al_2O_3 (M. Woelm, Eschwege) isolieren. Reine Metallcarbonyle wie das bei der Reaktion gebildete $Fe(CO)_5$ oder Reste von nicht umgesetztem $[Fe(CO)_4]_3$ werden mit dem Überschuss an Tolan zuerst mit Petroläther eluiert. Die Komplexe dagegen werden, ihrem jeweiligen Typ entsprechend, wesentlich stärker an aktivem Al_2O_3 absorbiert. Dies gilt besonders für die beiden Verbindungen $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ und (Tetracyclon)$Fe(CO)_3$, deren organischer Ligand eine Ketogruppe enthält. In Tabelle 3 sind die erhaltenen Komplextypen in der Reihenfolge aufgeführt, wie sie durch die angegebenen Lösungsmittel eluiert werden.

Die bei der Trennung anfallenden Lösungen werden im Vakuum zur Trockne gebracht und die erhaltenen Produkte aus Benzol–Petroläther oder Benzol–Methanol umkristallisiert. $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$, $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$, sowie $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ lassen sich auch durch Sublimation im Vakuum reinigen.

Bei der Reaktion entsteht etwas Hexaphenylbenzol, das hauptsächlich zusammen mit dem schwarzen $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ eluiert wird. Es kann durch fraktionierte Kristallisation abgetrennt werden. Tetracyclon dagegen lässt sich von der Chromatographiersäule vor dem roten $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ mit Benzol und wenig Äther eluieren.

* Die Analysen wurden von H. GEYER†, D. GRAF und R. HOUQUET ausgeführt.

[14] Dargestellt nach W. HIEBER, *Z. Anorg. Chem.* **204**, 165 (1932). Vgl. auch W. HIEBER u. G. BRENDEL, *Ibid.* **289**, 324 (1957).

TABELLE 3.—KOMPLEXVERBINDUNGEN AUS EISENTETRACARBONYL UND TOLAN

Komplex	Eluiert mit	Summenformel	Ausbeute[a] (g)	Analysen % berechnet C	H	O	Fe	Mol.-Gew.	% gefunden C	H	O	Fe	Mol.-Gew.
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)$	Petroläther	$C_{20}H_{10}O_6Fe_2$	1·2	52·45	2·20	20·96	24·39	458·0	52·44	2·22	21·09	24·42	468[c]
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$	CCl_4 oder Petroläther + 30% Benzol	$C_{34}H_{20}O_6Fe_2$	8·5	64·19	3·17	15·08	17·56	636·2	64·05	3·15	15·22	17·53	634[d]
$Fe(CO)_3(C_6H_5C_2C_6H_5)_2$	Benzol	$C_{31}H_{20}O_3Fe$	Spuren	75·01	4·07	9·67	11·25	496·35	75·12	4·07	9·87	11·31	516[e]
$Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$	Benzol	$C_{34}H_{20}O_6Fe_2$	8·5	57·80	2·70	17·11	22·40	748·1	57·84	2·78	17·04	22·39	700[c]
$Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$[b]	Äther	$C_{35}H_{20}O_7Fe_2$	3·5	63·29	3·03	16·86	16·82	664·2	63·26	3·06	17·11	16·96	646[c]
$Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2 \cdot 1/2\ C_6H_6$		$C_{39}H_{22}O_7Fe_2$		64·89	3·30	15·92	15·88	703·3	64·66	3·39	16·18	15·85	—
$Fe(CO)_4(C_6H_5C_2C_6H_5)_2$	Methanol oder Äthylacetat	$C_{32}H_{20}O_4Fe$	3·0	73·29	3·85	12·20	10·65	524·4	73·19	4·00	—	10·63	—

Bermerkungen: (*a*) Mittelwerte aus mehreren Ansätzen; (*b*) Kristallisiert ohne Verwendung von Benzol wie aus Aceton-Methanol; (*c*) Molekulargew.-Best. nach Hill-Baldes in Dioxan; (*d*) Ebulioskopisch in Benzol; (*e*) Nach Rast.

2. *Reaktionen der Komplexverbindungen*

(a) $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$

Abbau mit $LiAlH_4$. Zu einer Lösung von 1 g $LiAlH_4$ in 150 ml Tetrahydrofuran wird unter Rühren 0·5 g $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$, gelöst in wenig Tetrahydrofuran, langsam zugegeben. Nach einer Stunde wird das überschüssige Hydrid vorsichtig mit Wasser, dann mit Salzsäure zersetzt und die Reaktionslösung mehrmals mit Benzol extrahiert. Die vereinigten Benzolauszüge werden mit Wasser neutral gewaschen und getrocknet; sie ergeben neben 0·05 g nicht umgesetzter Komplexverbindung 0·3 g einer, in farblosen Nadeln kristallisierenden, organischen Verbindung vom F.P. 183–184°C. Sie ist mit 1:2:3:4-Tetraphenylbutadien[3] nach IR-Spektrum und Mischschmelzpunkt identisch und entsteht in 92% Ausbeute.

Abbau mit Natrium in flüssigem Ammoniak. Zu 3 g Natrium, gelöst in etwa 200 ml flüssigem Ammoniak, wird unter Rühren bei −60°C eine Lösung von 0·85 g $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ in 30 ml Tetrahydrofuran und 5 ml absolutem Äthanol schnell zugegeben. Man rührt noch eine Stunde, versetzt die Reaktionslösung mit Äthanol und lässt das Ammoniak verdampfen. Der Rückstand wird mit Wasser und Salzsäure behandelt und die organischen Reaktionsprodukte mit Benzol extrahiert. Sie ergeben nach Umkristallisieren aus Äthanol 0·34 g (55%) einer farblosen Substanz vom F.P. 95–100°C. Ihr IR-Spektrum ist identisch mit dem des in der Literatur[15] beschriebenen 1:2:3:4-Tetraphenylbutans vom F.P. 96°C. Gelegentlich erhält man auch eine andere Kristallform dieses niedrigschmelzenden 1:2:3:4-Tetraphenylbutans vom F.P. 85–88°C. Die IR-Spektren der beiden Modifikationen zeigen in KBr Abweichungen im Gebiet von 13–15 μ, sind aber in Lösung gleich.

Daneben entstehen beim reduktiven Abbau mit Natrium in flüssigem Ammoniak etwa 0·02 g des bei 185°C schmelzenden stereoisomeren 1:2:3:4-Tetraphenylbutans, das schon von anderen Autoren[3,16] beschrieben wurde. Dieses 1:2:3:4-Tetraphenylbutan kann auch dargestellt werden durch katalytische Hydrierung von 1:2:3:4-Tetraphenylbuten-1, bzw. 1:2:3:4-Tetraphenylbutadien an Raney-Nickel oder durch Umsetzung von 1:2-Diphenyläthylmagnesiumbromid mit 1:2-Diphenyläthylbromid in siedendem Äther.

(b) $Fe_2(CO)_6(C_6H_5C_2C_6H_5)$

Abbau mit Natrium in flüssigem Ammoniak. 0·18 g der roten Komplexverbindung, gelöst in 20 ml Äther und 5 ml absolutem Äthylalkohol, werden schnell in eine Lösung von 1 g Natrium in ca. 100 ml flüssigem Ammoniak gegeben. Man rührt noch etwa 10 Minuten bei −60°C und arbeitet die farblose Reaktionslösung wie unter (a) beschrieben auf. Es entsteht ausschliesslich Dibenzyl (F.P. 50°C), das durch sein IR-Spektrum charakterisiert wurde.

(c) $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$

Oxydation mit Brom in Eisessig. 0·5 g der gelben Komplexverbindung werden in 100 ml Eisessig gelöst und mit 1 g Brom versetzt. Nach längerem Stehen bei Zimmertemperatur entfernt man den Überschuss an Brom mit Na_2SO_3-Lösung. Extraktion

[15] E. BERGMANN, D. WINTER u. W. SCHREIBER, *Annalen* **500**, 128 (1933).
[16] E. S. WALLIS u. F. H. ADAMS, *J. Amer. Chem. Soc.* **55**, 3850 (1933).

mit Benzol und chromatographische Trennung liefern neben wenig Tetracyclon die Komplexverbindung (Tetracyclon)$Fe(CO)_3$ in hohen Ausbeuten.

Photolyse. In einem Quarzkölbchen werden 0·5 g des Komplexes in 150 ml Benzol gelöst und unter Luftabschluss mit einer UV-Lampe (125 W) belichtet. Nach 3 Stunden ist etwa die Hälfte der Verbindung abgebaut. Die chromatographische Aufarbeitung ergibt neben Tetracyclon hauptsächlich (1:2:3:4-Tetraphenylbutadien)-$Fe(CO)_3$.

Dieses *Tetraphenylbutadien-eisentricarbonyl* kristallisiert aus Alkohol oder Petroläther in langen, gelben Nadeln, die bei 230–232°C unter Zersetzung schmelzen. Das IR-Spektrum zeigt drei scharfe Absorptionsbanden bei 4·91, 5·05 und 5·13 μ für metallgebundene Kohlenoxydliganden.

Für $C_{31}H_{22}O_3Fe$ wird:

	C%	H%	O%	Fe%
berechnet:	74·71	4·45	9·64	11·21
gefunden:	74·69	4·39	9·72	11·25

Photolyse in Gegenwart von Schwefel. Belichtet man eine Lösung von 0·5 g der gelben Verbindung und 0·5 g Schwefel in 50 ml Benzol in einem Quarzkölbchen 16 Stunden mit einer UV-Lampe, so scheidet sich unter Kohlenoxydentwicklung ein brauner, eisenhaltiger Niederschlag ab, der nicht näher untersucht wurde. Die filtrierte Lösung wird eingedampft und überschüssiger Schwefel durch Kochen mit Natriumsulfidlösung entfernt. Mit Benzol lässt sich Tetraphenylthiophen (F.P. 184–185°C) als einziges organisches Reaktionsprodukt isolieren. Ausbeute: 0·15 g (49%).

Einwirkung von Kohlenoxyd unter Druck. Man lässt 2 g der gelben Komplexverbindung in Gegenwart von 7 ml Dekalin in einem 50 ml Rotierautoklaven mit Kohlenoxyd unter 200 at. vier Stunden bei 250°C reagieren. Die chromatographische Trennung des Reaktionsgemisches ergibt neben Eisenpentacarbonyl, 0·04 g Tetracyclon und *ca.* 1·5 g (Tetracyclon)$Fe(CO)_3$.

Abbau mit $LiAlH_4$. Zu einer Lösung von 1 g Komplex in 200 ml Äther wird unter Rühren eine Suspension von 0·9 g $LiAlH_4$ in 200 ml Äther zugegeben, das Gemisch eine Stunde bei Zimmertemperatur gerührt und anschliessend eine Stunde am Rückfluss erhitzt. Man arbeitet die Reaktionslösung wie unter (a) auf und erhält neben 0·04g unverändertem Komplex, 0·36 g (66%) einer farblosen, organischen Verbindung. Sie schmilzt bei 151–152°C und ist identisch mit 1:2:3:4-Tetraphenylbuten-1.[15]

In einem anderen Versuch wurde zu einer Lösung von 2 g $LiAlH_4$ in 100 ml Tetrahydrofuran eine Lösung von 2 g der Komplexverbindung im Laufe einer Stunde bei −8°C zugegeben und 20 Stunden bei 0°C gehalten. Die übliche Aufarbeitung ergab folgende Produkte: 0·22 g 1:2:3:4-Tetraphenylbuten-1 (20%), 0·44 g 1:2:3:4-Tetraphenylbutan vom F.P. 185°C (39%), wenig Tetraphenylbutadien-eisentricarbonyl und Spuren Tetracyclon.

Abbau mit Natrium in flüssigem Ammoniak. Eine Lösung von 3 g Natrium in etwa 250 ml flüssigem Ammoniak wird auf −60°C gekühlt. Nachdem man unter Rühren 1 g $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$, gelöst in Tetrahydrofuran, schnell zugegeben hat, werden sofort 15 ml absolutes Äthanol zugefügt.* Nach wenigen Minuten ist

* Die Zugabe von Äthanol zum Reaktionsgemisch ist wesentlich, da dadurch die reduzierende Wirkung des Systems erhöht wird.

die Reaktion beendet, und man erhält hauptsächlich 1:2:3:4-Tetraphenylbutan vom F.P. 185°C. Ausbeute: 0·21 g (37%).

Abbau mit Natriumamid in flüssigem Ammoniak. Eine farblose Lösung von Natriumamid in flüssigem Ammoniak, dargestellt aus 3 g Natrium, etwa 300 ml fl. NH_3 und wenig Eisennitrat, wird bei −60°C unter Rühren mit einer Tetrahydrofuranlösung von 0·5 g $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ langsam versetzt. Nach 15 Minuten arbeitet man die Reaktionslösung, wie unter (a) beschrieben, auf und erhält: 0·04 g 1:2:3:4-Tetraphenylbutadien (14%), 0·12 g Tetraphenylbutadien-eisentricarbonyl (31%), 0·3 g Tetracyclon (10%) und 0·09 g einer organischen Verbindung vom F.P. 218–220°C, die noch nicht näher untersucht wurde.

(d) $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$

Photolyse. Bestrahlt man 1 g der roten Komplexverbindung in 40 ml Toluol drei Stunden mit einer UV-Lampe (125 W), so kann man nach Abtrennung von 0·07 g eines braunen, eisenhaltigen Niederschlags aus dem Filtrat isolieren: 0·12 g des nicht umgesetzten Ausgangsproduktes, 0·48 g (Tetracyclon)$Fe(CO)_3$ (69%) und 0·02 g Tetracyclon.

Einwirkung von Kohlenoxyd unter Druck. In einem 0·5 L Autoklaven werden 3 g der roten Verbindung in 200 ml Petroläther (Kp. 80–90°C) bei einem Kohlenoxyddruck von 200 at. vier Stunden auf 170°C erhitzt. Die chromatographische Aufarbeitung des Reaktionsgemisches ergibt $Fe(CO)_5$, wenig Tetracyclon und 1·3 g (55%) (Tetracyclon)$Fe(CO)_3$.

Abbau mit $LiAlH_4$. In eine Lösung von 1 g $LiAlH_4$ in 250 ml Tetrahydrofuran gibt man langsam 1 g der roten Komplexverbindung, gelöst in 30 ml Tetrahydrofuran und arbeitet die Reaktionslösung nach einstündigem Rühren wie unter (a) beschrieben auf. Als Reaktionsprodukte werden erhalten: Tetracyclon, 2:3:4:5-Tetraphenylcyclopenten-2-on-1 (F.P. 163°C) und wenig einer orangefarbenen, organischen Verbindung vom F.P. 321°C. Diese ist mit dem von KVALNES[17] dargestellten Tetraphenyl-*p*-chinon nach Mischschmelzpunkt und IR-Spektrum identisch.

Abbau mit Natrium in flüssigem Ammoniak. Zu 2 g Natrium in 200 ml flüssigem NH_3 wird bei −60°C unter Rühren eine Lösung von 1 g $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ in 30 ml Tetrahydrofuran und 10 ml absolutem Äthanol schnell zugegeben. Dabei schlägt die tiefblaue Farbe der Lösung augenblicklich in rotbraun um. Die Aufarbeitung ergibt 0·05 g Tetraphenyl-*p*-chinon und 0·04 g einer noch nicht identifizierten Komplexverbindung, die bei 203–206°C unter Zersetzung schmilzt; im IR-Spektrum zeigt sie zwei scharfe Banden für die Absorption metallgebundener Kohlenoxydliganden. Daneben werden noch 0·04 g einer farblosen, organischen Substanz vom F.P. 320–326°C erhalten. Sie ist nach ihrem IR-Spektrum identisch mit Tetraphenylhydrochinon, das auch wie folgt dargestellt werden kann.

Tetraphenylhydrochinon. 0·01 g Tetraphenyl-*p*-chinon werden in 10 ml Dioxan mit einer konz. Lösung von $SnCl_2$ in konz. HCl auf dem Wasserbad erhitzt, bis sich die Lösung entfärbt. Nach Zugabe von Wasser wird mit Benzol extrahiert; aus Äther erhält man rautenförmige, farblose Kristalle von Tetraphenylhydrochinon, die bei 322–325°C schmelzen.

[17] D. E. KVALNES, *J. Amer. Chem. Soc.* **56**, 2476 (1934).

(e) $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$

Thermische Zersetzung. 0·75 g der schwarzen Komplexverbindung werden mit 30 ml Benzol im Bombenrohr 15 Stunden auf 150°C erhitzt. Unter Kohlenoxydentwicklung und Abscheidung von metallischem Eisen bildet sich $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ in etwa 75% Ausbeute. Wird die Zersetzung bei höheren Temperaturen durchgeführt (165°C), so entsteht neben $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$ auch (Tetracyclon)$Fe(CO)_3$.

Abbau mit $LiAlH_4$. Gibt man zu 4 g $LiAlH_4$ in 300 ml Tetrahydrofuran eine Lösung von 4 g der schwarzen Komplexverbindung in 100 ml Tetrahydrofuran, so färbt sich das Gemisch tiefrot und wird nach 1 1/2 Stunden Erhitzen am Rückfluss braun-schwarz. Die Aufarbeitung nach (a) ergab 1 g (51%) eines Gemisches aus wenig 1:2:3:4-Tetraphenylbuten-1 und 1:2:3:4-Tetraphenylbutan (F.P. 185°C).

Abbau mit Natrium in flüssigem Ammoniak. 2 g $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$, gelöst in 50 ml Tetrahydrofuran und 15 ml absolutem Äthanol, werden schnell in eine Lösung von 5 g Natrium in etwa 250 ml flüssigem Ammoniak bei −60°C gegeben. Die anfangs tiefblaue Farbe der Lösung schlägt sofort in braun um. Nach kurzem Rühren wird die Reaktionslösung nach (a) aufgearbeitet und ergibt neben 0·11 g nicht umgesetztem $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ etwa 0·37 g hochschmelzendes Tetraphenylbutan und 0·13 g (Tetraphenylbutadien)$Fe(CO)_3$.

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3. *Die Umsetzung von Eisentetracarbonyl mit Phenylacetylen*

(a) 2·5 g Eisentetracarbonyl[14] (0·005 Mol) und 3·3 ml Phenylacetylen (0·03 Mol) werden in einem Gemisch von 750 ml Petroläther (Kp. 60–65°C) und 100 ml Benzol etwa eine Stunde zum Sieden erhitzt, wobei man etwa 400–500 ml Lösungsmittel abdestilliert. Aus der filtrierten Reaktionslösung scheiden sich beim Stehen nach einigen Tagen schwarze, monokline Kristalle von $Fe_2(CO)_6(C_6H_5C_2H)_3$ ab. Ausbeute: *ca.* 0·5 g.

Der Komplex ist in organischen Lösungsmitteln nur wenig löslich, am geeignetsten sind noch Benzol, Dioxan, Tetrahydrofuran und CS_2. Zum Umkristallisieren löst man die feingepulverte Verbindung in möglichst wenig warmem Benzol und gibt die 10-fache Menge an heissem Petroläther zu.

Für $C_{30}H_{18}O_6Fe_2$ wird:

	C%	H%	O%	Fe%
berechnet:	61·47	3·09	16·38	19·06
gefunden:	61·34	3·13	16·43	18·97

Die Mutterlauge des schwarzen Komplexes enthält noch andere Komplexverbindungen, die chromatographisch über aktives Al_2O_3 und fraktionierte Kristallisation getrennt werden können.

(b) 10 g Eisentetracarbonyl (0·02 Mol) werden mit 100 ml Phenylacetylen unter Rühren auf 75°C erhitzt.* Unter Entwicklung von nahezu 1 Mol Kohlenoxyd pro Mol $[Fe(CO)_4]_3$ und Bildung von Eisenpentacarbonyl setzt eine Reaktion ein, die nach etwa 30 Minuten beendet ist. Der Überschuss von Phenylacetylen und das entstandene $Fe(CO)_5$ werden im Vakuum abdestilliert, die zurückbleibenden Komplexverbindungen (*ca.* 20 g) in CS_2 gelöst und durch Chromatographie über saurem

* Bei einer Reaktionstemperatur von 60°C dauert die Umsetzung etwa 3 Stunden. Bei 80°C verläuft die Reaktion exotherm und ist in wenigen Minuten beendet.

TABELLE 4.—KOMPLEXVERBINDUNGEN AUS EISENTETRACARBONYL UND PHENYLACETYLEN

Komplex	Farbe	Eluiert mit	Kristallisiert aus	Summenformel	Analysen									
					% berechnet					% gefunden				
					C	H	O	Fe	Mol.-Gew.	C	H	O	Fe	Mol.-Gew.
$Fe_2(CO)_6(C_6H_5C_2H)_3$	orange	Petroläther	Äthanol	$C_{32}H_{18}O_6Fe_2$	54·59	2·50	19·83	23·08	484·0	54·64	2·65	19·79	23·21	426[a]
$Fe(CO)_4(C_6H_5C_2H)_5$	orange	Benzol	Benzol	$C_{44}H_{30}O_4Fe$	77·88	4·46	9·43	8·23	678·6	77·80	4·45	9·83	8·34	650[a]
$Fe(CO)_3(C_6H_5C_2H)_4$	violett	Benzol	Tetrahydrofuran	$C_{36}H_{24}O_3Fe$	76·65	4·41	8·75	10·19	548·4	76·57	4·41	—	10·44	—
$Fe(CO)_4(C_6H_5C_2H)_3$	orange	Benzol und Äther	Benzol + Petroläther	$C_{28}H_{18}O_4Fe$	70·90	3·83	13·49	11·78	474·3	70·79	3·93	13·60	11·82	429[b]
$Fe(CO)_3(C_6H_5C_2H)_3$	rot	Benzol und Äther	Benzol + Petroläther	$C_{28}H_{18}O_4Fe$	70·90	3·83	13·49	11·78	474·3	71·24	3·92	13·69	11·76	464[b]
$Fe(CO)_4(C_6H_5C_2H)_2$	gelb	Methanol	Äthanol	$C_{20}H_{12}O_4Fe$	64·55	3·25	17·20	15·00	372·2	64·28	3·04	17·26	14·76	370[a]

Bermerkungen:
(*a*) Ebulioskopisch in Benzol; (*b*) Kryoskopisch in Benzol.

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Al_2O_3 in die einzelnen Verbindungen getrennt. In Tabelle 4 sind die einzelnen Komplextypen in der Reihenfolge angegeben, in der sie sich mit den bezeichneten Lösungsmitteln eluieren lassen. Von den bei der Umsetzung als Nebenprodukte entstehenden organischen Verbindungen wird 1:2:4-Triphenylbenzol zusammen mit $Fe_2(CO)_6(C_6H_5C_2H)_2$ eluiert und kann durch Umkristallisieren abgetrennt werden.

Eine einmalige chromatographische Trennung führt bei den Komplexverbindungen aus Phenylacetylen nicht unmittelbar zu den reinen Substanzen. Es ist erforderlich, die einzelnen Fraktionen erneut zu chromatographieren oder durch fraktionierte Kristallisation weiter zu reinigen. Aus Tabelle 4 sind die zum Umkristallisieren der einzelnen Komplexe geeigneten Lösungsmittel ersichtlich. $Fe_2(CO)_6(C_6H_5C_2H)_2$ und $Fe(CO)_4(C_6H_5C_2H)_2$ lassen sich auch durch Sublimation im Vakuum rein erhalten.

4. *Die Umsetzung von* $Fe(CO)_4(C_6H_5C_2H)_2$ *mit Tolan*

0·5 g des gelben Komplexes werden mit einem grossen Überschuss (3 g) Tolan 1·5 Stunden auf *ca.* 200–230°C erhitzt. Unter Braunfärbung des Reaktionsgemisches beobachtet man eine langsame Gasentwicklung. Am Ende erhitzt man noch kurze Zeit auf 250–260°C. Nach dem Erkalten wird der Kolbeninhalt in Benzol gelöst, mit 2n HCl gewaschen, getrocknet und chromatographisch vorgereinigt. Die farblose Fraktion enthält Tolan, Hexaphenylbenzol und 1:2:3:4-Tetraphenylbenzol (0·04 g), das durch fraktionierte Sublimation aus diesem Gemisch isoliert wird. Es schmilzt nach Umkristallisieren aus Äthanol bei 183–193°C und ist nach dem IR-Spektrum identisch mit dem von DILTHEY u. HURTIG[18] dargestellten 1:2:3:4-Tetraphenylbenzol (F.P. 191°C).

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ZUSAMMENFASSUNG

Die Umsetzung von Eisentetracarbonyl mit Alkinen führt in einer einfachen Reaktion zu verschiedenen Typen von Organoeisencarbonyl-Verbindungen. Als organische Liganden dieser π-Komplexe treten Doppelbindungssysteme auf, die sich aus der eingesetzten Acetylenkomponente in stereospezifischer Weise bilden. Dabei erhält man auch Verbindungstypen, bei denen Kohlenoxyd aus dem Metallcarbonyl in das Skelett des organischen Teils als Ketogruppe eingebaut ist. Diese Anlagerung von Kohlenoxyd an die Alkine erfolgt nach den bisherigen Ergebnissen an demjenigen Kohlenstoffatom der Dreifachbindung, dessen Substituent den grösseren negativen, mesomeren Effekt ausübt.

Wie bei der Beschreibung der einzelnen Komplexverbindungen gezeigt wurde, lassen sich durch geeignete Umsetzungen gesättigte und ungesättigte Kohlenwasserstoffe, Ringketone, Chinone, sowie aromatische und heterocyclische Verbindungen erhalten.

Diese Untersuchungen wurden im Rahmen eines Forschungsprogramms ausgeführt, das durch die Union Carbide Corporation, New York, unterstützt wird. Der Direktion der European Research Associates, Brüssel, danken wir für die grosszügige Förderung unserer Arbeit. Die Messungen der Röntgen-*K*-Absorptionskante sowie die magnetischen Untersuchungen wurden durch das Physikalische Institut der Technischen Hochschule München ausgeführt, wofür wir HERRN PROF. DR. G. JOOS besonders danken.

[18] W. DILTHEY u. G. HURTIG, *Ber. Dtsch. Chem. Ges.* **67**, 2004 (1934).

Anmerkung bei der Korrektur: Inzwischen erschienen zwei kurze Mitteilungen von SCHRAUZER,[19] in welchen (Tetracyclon)$Fe(CO)_3$ und (2:5-Diphenyl-cyclopentadienon)-$Fe(CO)_3$ ebenfalls beschrieben werden. Zusammensetzung und Struktur der dort weiterhin erwähnten rubinroten Verbindung $Fe(CO)_4(C_6H_5C_2C_6H_5)$ halten wir für unwahrscheinlich; die Substanz dürfte identisch sein mit der Komplexverbindung $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ (vgl. Tabelle 1 und 3).

[19] G. N. SCHRAUZER, *Chem. & Ind.* 1403, 1404 (1958).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 269 to 274. Pergamon Press Ltd. Printed in Northern Ireland

CATALYTIC RACEMIZATION OF OPTICALLY ACTIVE COMPLEXES: TRIS(ETHYLENEDIAMINE)COBALT(III), -PLATINUM(IV), AND -RHODIUM(III) HALIDES

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Abstract—Catalytic racemization of tris(ethylenediamine)cobalt(III) iodide has been studied in the presence of active carbon, platinum black and silica gel. Exchange studies of the cobalt complex with the ^{14}C-labelled ethylenediamine indicate that the complex first is activated and then racemizes. This process is accompanied by partial decomposition of the complex. Catalytic racemization of tris(ethylenediamine)platinum(IV) and -rhodium(III) also has been studied in the presence of active carbon, platinum black, and silica gel. Exchange studies of the platinum compound with ^{14}C-labelled ethylenediamine were made under experimental conditions similar to those for racemization. No exchange was found to occur during the process. The racemization most probably takes place through an activated six-co-ordinate intermediate.

ALTHOUGH the tris(ethylenediamine)cobalt(III) cation, $[Co(en)_3]^{3+}$, is remarkably inert in aqueous solution[1] it is racemized under forcing conditions: 70° and the presence of a great excess of ethylenediamine.[2] Further, when solutions of optically active tris(ethylenediamine)cobalt(III) chloride are heated with activated carbon at 90°, they become optically inactive within 5 min. The absorption spectrum of the solution after treatment is the same between 330 mμ and 725 mμ as the original sample.[3] It was of interest to determine whether the tris(ethylenediamine)cobalt(III) ion behaves similarly with other catalysts, such as platinum black and silica gel, and whether the tris(ethylenediamine) ions of platinum(IV) and rhodium(III) are similarly racemized. Also any insight into the mechanism of racemization was desirable.

EXPERIMENTAL

Preparations. Tris(ethylenediamine)cobalt(III) chloride was prepared by the method of WORK[4] and resolved by the fractional crystallization of the chloro-*d*-tartrate salt.[1a] Since the L-chloro-*d* tartrate is much less soluble, it can be obtained in the pure state very easily by fractional crystallization. The L-chloro-*d*-tartrate was then treated with hot saturated KI solution whence $[Co(en)_3]I_3$ precipitated out of the solution in fine needles. The specific rotation for the iodide with sodium light was $-154°$ which is almost equal to the value obtained by WERNER ($-155°$). The optical rotations were measured with a Schmidt-Haensch double field polarimeter which read to $\pm 0{\cdot}01°$ by means of the vernier scale.

The tris(ethylenediamine)platinum(IV) chloride was made by the method of WERNER[5] and resolved into its dextro and laevo forms by the fractional crystallization of the chloro-*d*-tartrate salt by adding *d*-NH_4-tartrate to the racemic mixture of the platinum compound. The L-$[Pt(en)_3]^{Cl_4}_{d\text{-}T_4H_4O_6}$ which precipitated was filtered and recrystallized. The compound was then treated with a hot,

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[1a] A. WERNER, *Ber. Dtsch. Chem. Ges.* **45**, 121 (1912); [1b] For other references see the review by F. BASOLO, *Chem. Rev.* **52**, 459–527 (1953).
[2] W. G. GEHMAN and W. C. FERNELIUS, *J. Inorg. Nucl. Chem.* **9**, 71 (1959).
[3] B. E. DOUGLAS, *J. Amer. Chem. Soc.* **76**, 1020 (1954).
[4] J. B. WORK, *Inorganic Syntheses* Vol. 2, p. 221. McGraw-Hill, New York (1946).
[5] A. WERNER, *Naturf. Ges. Zürick* **62**, 553 (1917).

saturated solution of potassium iodide causing the precipitation of L[Pt(en)$_3$]I$_4$. This was then reconverted to chloride by treating with silver chloride.

Tris(ethylenediamine)rhodium(III) chloride was prepared by the method of WERNER.[6] The dextro and the laevo compounds were separated by fractional crystallization of the chloride-tartrate compound. L-[Rh(en)$_3$]$^{Cl}_{d\text{-}C_4H_4O_6}$ separated out first and was further purified by fractional crystallization from hot water. The product was then decomposed by adding hot, saturated potassium iodide solution to a concentrated solution of the chloride-tartrate compound. The specific rotation of the chloride-tartrate was found to be $[\alpha]_D^{25} = -48°$ which is very near to value obtained by WERNER, ($[\alpha]_D^{25} = -50°$).

Racemization. The racemization studies were made as follows: 15 ml of a solution of [Co(en)$_3$]I$_3$ in a conical flask with reflux condenser was heated to the desired temperature. Then the charcoal (platinum black or silica gel) was added to the solution and kept at that temperature for the desired time. At the end of the period, the flask was removed from the heat source and the solution filtered from charcoal through a quick-filtering filter paper. Then it was again filtered, this time through a No. 42 Whatman filter paper to remove any charcoal particles which may have escaped previous filtration. The solution was then evaporated under an infra-red lamp and weighed to determine the amount of compound that had been absorbed by charcoal. When complete racemization occurred no evaporation was performed. The activity of the treated compound was then determined in the polarimeter.

Exchange between the complex and ^{14}C *labelled ethylenediamine.* Labelled ethylenediamine dihydrochloride prepared by Dr. W. G. GEHMAN[2] was used for all the exchange experiments. An aqueous solution of [Co(en)$_3$]I$_3$ and labelled ethylenediamine hydrochloride were mixed together and heated to the temperature of the racemization experiment. Activated carbon was then added and the heating continued for the desired time. The solution was then filtered and [Co(en)$_3$]I$_3$ was precipitated from the filtrate by the addition of saturated potassium iodide solution.

The manipulation of the solid precipitate was carried out as follows: A Büchner funnel with sintered glass base was sawed apart, flush with the top surface of the sintered disk. The two portions were then ground with carborundum to give a smooth fit. A piece of filter paper (Schleicher and Schuell No. 576) was placed on the sintered disk and the glass chimney replaced. After filtration, the filter paper was removed for drying, counting and weighing.[7]

For counting purposes the filter paper with the precipitate was mounted between two aluminium plates, one of which was solid and the other had a hole in the centre with slightly smaller diameter than the filter paper. The activities were counted with a scaling unit made by Nuclear Instrument and Chemical Corp. (Model 165) and a Geiger–Müller counting tube with a 2·88 mg/cm^2 window thickness (made by Dr. W. W. MILLER).

Spectrophotometric studies. Spectrophotometric studies were done in a Beckman DU model quartz spectrophotometer. The absorption curves of the original solution of [Co(en)$_3$]I$_3$ as well as of those which were treated with activated charcoal for the racemization reaction were studied at various experimental conditions.

Activated charcoal. A quantity of powdered wood charcoal (Fisher Scientific) was activated by the following treatment. The charcoal was first refluxed with concentrated hydrochloric acid for about 6 hr. It was then filtered and thoroughly washed with water to remove hydrochloric acid. It was dried and finally heated to 700° in a loosely covered crucible for about 2 hr. It was then cooled and bottled in a stoppered bottle. This charcoal usually remained active for months.

Platinum black. Potassium chloroplatinate solution was warmed on a water bath with alcohol and a little potassium hydroxide solution. The black precipitate was filtered, washed thoroughly with water and dried.

Silica gel. The silica gel was heated to about 200° for 3 hr, cooled and kept in a desiccator over concentrated sulphuric acid.

RESULTS AND DISCUSSION

Studies on [Co(en)$_3$]$^{3+}$. It has been found that optically active [Co(en)$_3$]Cl$_3$ when treated with activated charcoal loses its optical activity very easily. On the other hand,

[6] A. WERNER, *Ber. Dtsch. Chem. Ges.* **45**, 1229 (1912).
[7] M. CALVIN, C. HEIDELBERGER, J. C. REID, B. M. TOLBERT and P. F. YANKWICH, *Isotopic Carbon* p. 115. John Wiley, New York (1949).

it has been pointed out by various workers[1] that without activated charcoal this compound can be boiled for hours without any loss of optical activity, and a solution of $[Co(en)_3]Cl_3$ remains for months without any noticable change in optical rotation.

As pointed out by DOUGLAS, it is not possible to analyse mathematically any of the data available from the charcoal treatment. The charcoal loses most of its activity within a few minutes and it is almost impossible to know how much of the activated charcoal has become inactive at a particular time.

The case of the exchange studies was similar. The activated charcoal adsorbed

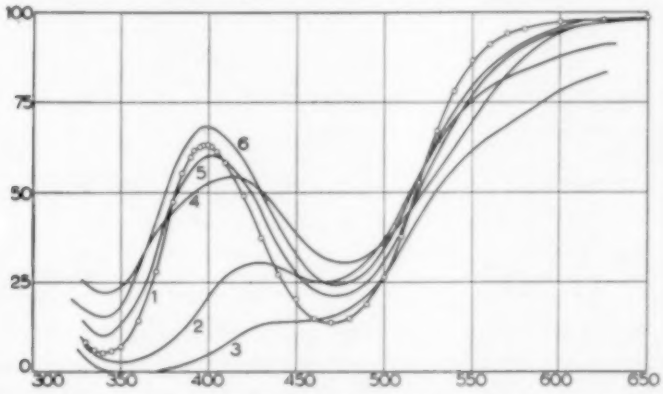


FIG. 1.—Absorption spectra of $[Co(en)_3]I_3$ and its reaction products. 1—Original solution; 2—Boiling for 5 min in the presence of charcoal; 3—Racemized by boiling for 10 min with charcoal; 4—Boiling for 20 min with platinum black; 5—Racemized by boiling for 10 min with platinum black; 6—Heating at 80° for 15 min in presence of charcoal.

considerable radioactive ethylenediamine and the amount adsorbed was dependent on the temperature of the reaction and the amount of charcoal and ethylenediamine added. However, an attempt has been made to calculate the amount of exchange by subtracting the total amount of ethylenediamine adsorbed by charcoal. This gives the order of magnitude of the exchange reaction though not the exact values.

When the complex is boiled in the presence of charcoal for about 5 min and then filtered, a definite colour change is observed. The colour of the solution first changes from yellow to reddish brown. This points to the possibility of the formation of a bis(ethylenediamine)aquo complex of cobalt(III). To settle this point the absorption spectra of the original complex salt solution and the solution after treatment with active carbon at different temperatures and different time lengths were studied. These are shown in Fig. 1. It is found from the study of the curves that the sample which was boiled for 10 min in the presence of charcoal is definitely decomposed and most probably has been converted into a bis(ethylenediamine)aquohydroxocobalt(III) complex. The sample which has been boiled for 5 min shows less of a shift from the original curve. The sample which was heated to 80° for 15 min is little decomposed as seen from the curve. However, all these three samples underwent complete racemization. It is to be concluded from the above observations that although the racemization can take place without decomposition, there is a definite tendency for the compound to undergo decomposition under these experimental conditions.

The study of the exchange reaction with radioactive ethylenediamine showed that, in every case, a considerable amount of exchange took place. The sample which was

boiled for 10 min gave a 15 per cent exchange after treatment with active carbon when it is calculated on the basis that the complex is the tris(ethylenediamine) compound. When calculated as the bis(ethylenediamine) compound one gets 18 per cent exchange. The sample heated to 80° for 15 min gives an exchange of 22 per cent (calculated as the tris(ethylenediamine) compound).

TABLE 1

Catalyst used	Reaction time (min)	Reaction temp (°C)	Exchange (%)
Charcoal (active)	10	100	15
Charcoal (active)	15	80	22
Pt. black	75	100	28

Similar observations were made both spectrophotometrically and in exchange reactions when the complex was treated with platinum black, though to a lesser extent. The exchange observed here was 27·7 per cent only when boiled for 75 min. Considering the above facts, it seems that the racemization processes involved in these two cases are similar. The optically active complex when similarly boiled with silica gel does not lose any optical activity.

Under the experimental conditions, the racemization can take place according to any of the following schemes:

(1) Simple dissociation and subsequent decomposition of the tris(ethylenediamine) compound to form bis(ethylenediamine)aquo compound.

(2) Intramolecular dissociation with five-co-ordinate intermediate.

(3) Activated six-co-ordinate intermediate without bond rupture.

By process (1), the complex can first decompose to form a bis(ethylenediamine)-aquo complex. The tendency for the decomposition of the complex was noticed when the complex was boiled for 10–15 min in the presence of active carbon. By this process, the complex can lose its optical activity, only by decomposition.

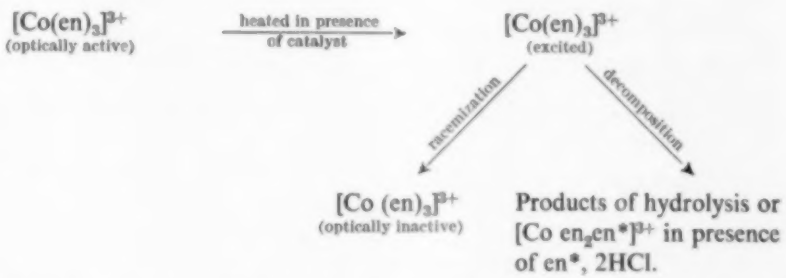
By the second method, one of the links of the ethylenediamine molecule may be broken. The complex ion can rearrange causing the loss of optical activity. Under this condition no exchange is expected. However, another ethylenediamine molecule may take up the vacant co-ordination position and displace one of the former ethylenediamine molecules. Under these conditions, exchange and racemization may take place together and they will depend on one another. The place of the attacking en molecule may also be taken up by water, whence the whole process will resemble (1)—the H_2O occupying the vacant position first and then, by knocking out the loosely bound ethylenediamine, will form the bis(ethylenediamine)aquocobalt complex.

There should not be any bond rupture if the racemization takes place by the third postulated method. A substance that autoracemizes, but gives no indication of bond rupture will be expected to undergo racemization via an activated intermediate. That

the intermediate should have more energy follows from the fact that the two enantiomorphic forms have the same energy but only slowly lose their optical activity. An example of this type of racemization has been given by RÂY and DUTT[8] for tris(biguanidide)cobalt cation which slowly racemizes on heating a solution of the pure salt. However, the evidence of bond rupture does not exclude the intramolecular rearrangement mechanism since racemization may proceed by a different mechanism than decomposition or exchange.

In the case of tris(ethylenediamine)cobalt(III) there is no sign of autoracemization. From the spectrophotometric investigation it has been observed that there is a definite tendency for bond rupture in the process, though it has been found that racemization and decomposition of the complex do not go side by side and they are not interdependent. If the racemization took place by any kind of bond rupture, a much higher exchange of ethylenediamine would have been expected. It has been found that when the racemization is complete, the exchange is only 20 per cent.

Under this condition the following mechanism is suggested for the racemization of $[Co(en)_3]^{3+}$ in the presence of charcoal and platinum black.



The excited state of the $[Co(en)_3]^{3+}$ is attained by the third postulated mechanism, the heat and the active carbon supplying the energy. In all probability there is no sharp line dividing the complete racemization process without any decomposition and with decomposition. The energy supplied by heat and charcoal may be sufficient to cause both the reactions to go on simultaneously.

Studies on $[Pt(en)_3]^{4+}$ *and* $[Rh(en)_3]^{3+}$. Tris(ethylenediamine)platinum(IV) ion was found to be optically very stable. The aqueous solution of this was boiled for about 6½ hr without any change in optical rotation. It was then heated with activated charcoal. In 5 min there was no change in rotation. Boiling for 30 min caused little diminution in the optical rotation, although in 70 min the complex was completely racemized. Boiling with platinum black for 3 hr caused no diminution in optical rotation. Boiling with silica gel for a number of hours did not produce any racemization. Moreover, $[Rh(en)_3]Cl_3$, was not found to be effected by boiling alone, or boiling with activated charcoal, platinum black, and silica gel. The optical rotation remained completely unaffected by any treatment.

Exchange of the labelled ethylenediamine with the complex ion in the presence of activated charcoal was studied. It was found that the exchange takes place to a very slight extent which may easily pass for contamination. If there are any decomposition or dissociation processes involved in the racemization, it is expected that a large amount

[8] P. RÂY and N. K. DUTT, *J. Indian. Chem. Soc.* **20**, 81 (1943).

of exchange with ^{14}C-labelled ethylenediamine, available in the system in the exchange study experiments, will take place during racemization. On the contrary, very little exchange is found. STEIGMAN[9] studied the exchange of tris(ethylenediamine) complexes of Rh, Ir and Pt with radiometals derived by a Szilard–Chalmers reaction. He found a slow exchange in all cases. Hence, a little exchange is expected in the exchange studies with $[Pt(en)_3]^{4+}$ and labelled en, independent of any racemization process.

Under the conditions of the present experiments, it is concluded that the racemization of optically active $[Pt(en)_3]^{4+}$ in the presence of activated charcoal takes place via activated six-co-ordinate intermediate formation without any bond rupture.

$$[Pt(en)_3]^{4+}_{\text{(optically active)}} \longrightarrow \text{Heated in presence of catalyst} \longrightarrow [Pt(en)_3]^{4+}_{\text{(excited)}} \xrightarrow{\text{racemization}} [Pt(en)_3]^{4+}_{\text{(optically inactive)}}$$

The charcoal catalyst supplied the energy for excitation. However, platinum black and silica gel were found to be completely inactive in the racemization of the complex, In the case of $[Rh(en)_3]^{3+}$ complex, even activated charcoal was found not to be effective.

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[9] J. STEIGMAN, *Phys. Rev.* **59**, 498 (1941).

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THE PREPARATION AND INFRA-RED ABSORPTION SPECTRA OF SEVERAL COMPLEXES OF BIS-(2-ETHYLHEXYL)-PHOSPHORIC ACID*

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Abstract—The bis-(2-ethylhexyl)-phosphates† of Li(I), Na(I), K(I), $Co(NH_3)_4$(III), $Co(en)_3$(III), Sc(III), Zr(IV), Hf(IV), Th(IV), and U(VI) have been prepared. The mixed nitrate-bis-(2-ethylhexyl)-phosphates of Zr(IV), Hf(IV), Ce(IV), Ce(IV), and Th(IV) were also prepared. The infra-red absorption spectra of all these compounds were obtained, and the antisymmetric POO^- stretching vibrations were compared. The POO^- stretching vibration frequencies of the bis-(2-ethylhexyl)-phosphates of Sc(III) and Th(IV) were found to be similar to those found for the alkali metal salts and cobaltic salts, indicating high ionic character of the metal to oxygen bond of the phosphate. The bonding to the phosphate of the Hf(IV) and Zr(IV) complexes appears to be of a more covalent character. It is concluded that the nitrate in the mixed compounds is co-ordinated to the metal atom and that the metal-to-nitrate bond is essentially covalent. The bonding to the phosphate in the mixed compounds appears to be different from that in the pure phosphates.

Recently the organophosphoric acids have been demonstrated to have interesting solvent properties for various inorganic salts. In particular HDEHP[1-6] has been the subject of several studies in this laboratory and others. The present study involves the extraction from neutral aqueous solutions of the chlorides and nitrates of Sc(III), Zr(IV), Hf(IV), Th(IV), Ce(IV) and U(VI) by HDEHP. The complexes formed in the saturated solutions were determined, and their infra-red spectra were investigated. For comparison, the salts of HDEHP with Li(I), Na(I), K(I), $Co(en)_3$(III) and $Co(NH_3)_4$(III) were also prepared and their infra-red spectra obtained.

EXPERIMENTAL

Purification of HDEHP

The purification of HDEHP has been reported in a previous publication.[6]

Preparation of the bis-(2-ethylhexyl)-phosphates

(a) NaDEHP. A solution of 2 g of HDEHP in 100 ml of di-*n*-butyl ether was shaken for 3 min with 25 ml of 1 N NaOH. The mixture was centrifuged and the phases separated. Upon evaporation of the solvent in the organic phase, a grey-white waxy slush was obtained. A DEHP/Na formal ratio of 0·95 was found by analysis.

(b) KDEHP. The potassium salt of HDEHP was prepared as in the procedure for NaDEHP. A formal ratio DEHP/K of 1·0 was found by analysis.

(c) LiDEHP. The lithium salt of HDEHP was prepared as in the procedure for NaDEHP. A DEHP/Li formal ratio of 0·99 was found by analysis.

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† Henceforth bis-(2-ethylhexyl)-phosphoric acid will be abbreviated as HDEHP.

(1) D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
(2) D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
(3) D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **4**, 141 (1957).
(4) C. F. BAES, JR., R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).
(5) D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).
(6) D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).

(d) $[Co(en)_3](DEHP)_3$. To 100 ml of di-*n*-butyl ether was added 2 g of HDEHP, and this mixture was contacted for 3 min with a solution of 0·75 g of $[Co(en)_3]Cl_3$ in 6·5 ml of 1 N NaOH. The phases were separated and the organic phase contacted twice with 65 ml portions of water each containing 0·75 g of $[Co(en)_3]Cl_3$. The mixture was centrifuged and the phases separated. Upon evaporation of the solvent in the organic phase a brown oil was obtained. A DEHP/Co formal ratio of 3·03 was found by analysis.

(e) $[Co(NH_3)_6](DEHP)_3$. To 100 ml of di-*n*-butyl ether was added 4·2 g of HDEHP, and this mixture was contacted for 2 min with a solution of 1·5 g of $[Co(NH_3)_6]Cl_3$ in 13 ml of 1 N NaOH. The phases were separated and the organic phase was scrubbed twice more with an aqueous solution of 1·5 g $[Co(NH_3)_6]Cl_3$. The mixture was centrifuged and the phases separated. Upon evaporation of the solvent in the organic phase an orange-yellow solid was obtained. The formal ratio of DEHP/Co was found to be 3·08 by analysis.

(f) *Thorium.* A solution of 2 g of HDEHP in 100 ml of toluene was contacted with 7·0 ml of $ThCl_4$ solution (0·70 g Th/ml) for 3 min. The phases were separated, and the organic phase was contacted three more times with the $ThCl_4$ solution using 7·0 ml aliquots each time. The mixture was centrifuged and the organic phase washed several times with distilled water. Upon evaporation of the toluene in the organic phase a white waxy solid was obtained. A formal ratio of DEHP/Th was found to be 3·90 by analysis. It was determined by alkali titration that the combined water phases contained four acid equivalents per atom of Th extracted.

(g) *Scandium.* The scandium complex of bis-(2-ethylhexyl)-phosphoric acid could be prepared using $ScCl_3$ or $Sc(NO_3)_3$, and both procedures will be described.

A solution of 10·2 g of HDEHP in 100 ml of toluene was contacted for 3 min with 39·90 ml of an aqueous $ScCl_3$ solution (0·014 g Sc/ml). The mixture was centrifuged. The phases were separated and the organic phase given one additional pass with the $ScCl_3$ solution; however the organic phase was found to have been saturated with the first pass, since the scandium of the second pass could be quantitatively recovered in the aqueous phase. The phases were separated, and the organic phase was washed several times with distilled water. It was observed that with even one pass of the $ScCl_3$ solution some solid material separated from the solution and collected at the liquid interface. Water washes of the organic phase also caused this solid deposition. A white waxy solid was obtained upon evaporation of the solvent. A DEHP/Sc formal ratio of 2·8 was obtained by analysis.

A solution of 2 g of HDEHP in 200 ml of toluene was contacted for 3 min with a $Sc(NO_3)_3$ solution (0·0868 g Sc total.) A similar solid phase at the interface was observed as in the above preparation. The mixture was centrifuged and the phases separated. The organic phase was contacted with a second portion of the above $Sc(NO_3)_3$ solution. The mixture was centrifuged and the phases separated. A solid separated from the organic phase when it was washed several times with distilled water. A DEHP/Sc formal ratio of 2·6 was established for the material obtained upon evaporation.

(h) *Zirconium.* A solution of 4 g of HDEHP in 100 ml of toluene was contacted three times (3 min each) with 25 ml portions of an aqueous solution containing 80 mg of $ZrCl_4$ per ml. No separation of solid occurred. The mixture was centrifuged and the phases separated. The organic phase was washed twice with water and allowed to evaporate. A white waxy solid was obtained. A formal ratio (DEHP/Zr) of 4·0 was found by analysis.

(i) *Hafnium.* A solution of 2 g of HDEHP in 100 ml of toluene was contacted for 3 min with 50 ml of a $HfCl_4$ solution (88 mg/ml of $HfCl_4$). No solid material separated out. The phases were separated and the organic phase given three additional passes with $HfCl_4$ solution. The mixture was centrifuged and the phases separated. The organic phase was scrubbed twice with water and then allowed to evaporate. A white waxy solid was obtained. A DEHP/Hf formal ratio of 3·7 was obtained by analysis.

(j) $UO_2(DEHP)_2$.[4] A solution of 2·2 g of HDEHP in 100 ml of toluene was scrubbed for 3 min with an aqueous solution containing 2·5 g of $UO_2(NO_3)_2 \cdot 6H_2O$. A second pass was made, and solid began to separate out. The phases were separated and the organic phase water washed. The organic phase was then allowed to evaporate. A yellow waxy solid was obtained. The formal ratio of DEHP/U was found to be 1·99. This preparation confirms the work of BAES *et al.*[4]

Preparation of the mixed nitrate bis-(2-ethylhexyl)-phosphates

(a) $[ZrO_{0.5}(NO_3)(DEHP)_2]_n$. A solution of 5 g of HDEHP in 50 ml of toluene was scrubbed for 3 min with 25 ml of an aqueous solution containing 70 mg of zirconium nitrate per ml. No solid phase

separated out. The phases were separated and the organic phase given three additional passes with 25 ml portions of the above solution. The mixture was centrifuged and the phases separated. The organic phase was washed several times with water and allowed to evaporate. A white waxy solid was obtained. The formal ratio of NO_3/Zr for different preparations was found by analysis to be 0·6–1·2 and that of DEHP/Zr was 1·8–2·2.

(b) $Hf(NO_3)(DEHP)_3$. A solution of 4·3 g of HDEHP in 100 ml of toluene was contacted for 3 min with 40 ml of a solution containing 80 mg of hafnium nitrate per ml. The organic phase was separated, and scrubbed with the hafnium solution. No solid separated out. The phases were centrifuged, separated, and the organic phase was allowed to evaporate. A white waxy solid was obtained. The formal ratio of NO_3/Hf was found to be 1·2 ,and that of DEHP/Hf was 3·1.

(c) $Th(NO_3)(DEHP)_3$. A solution of 2 g of HDEHP in 100 ml of toluene was contacted with 9·00 ml of $Th(NO_3)_4$ solution (0·044 g Th/ml) for 3 min. The mixture was centrifuged and the phases separated. The organic phase was contacted with two additional 9·00 ml aliquots of the $Th(NO_3)_4$ solution. The aqueous solutions were combined and titrated for acid using standard sodium hydroxide, after addition of KF to complex the thorium. The organic phase was washed several times with distilled water. Upon evaporation of the toluene in the organic phase a white waxy solid was obtained. The formal ratio of DEHP/Th was found by analysis to be 2·8, while that of the NO_3/Th was 1·06. It was determined by alkali titration that the water phase contained three acid equivalents per atom of Th extracted.

(d) $[CeO_{0\cdot5}(NO_3)(DEHP)_2]_n$. A solution of 4 g of HDEHP in 100 ml of toluene was contacted for 3 min with 20 ml of a saturated aqueous solution of $(NH_4)_2Ce(NO_3)_6$. Some solid separated. The liquid phases were separated and the organic phase again contacted with a 25 ml portion of solution of the above composition. Some additional solid separated. The mixture was separated and the clarified organic phase allowed to evaporate. A yellow waxy solid was obtained. The formal ratio of NO_3/Ce was found to be 1·0 and that of DEHP/Ce was 2·1.

Analytical procedures used

The water analyses on these compounds were made by the Karl Fischer titration method. The phosphorus analyses involved refluxing of the compounds with fuming H_2SO_4 and $HClO_4$ and subsequent determination colorimetrically by the use of ammonium vanadate and ammonium molybdate.[7,8] The nitrogen analyses were made by a modified Kehldahl method[9] (reduction to ammonia by Ag_2SO_4 and $FeSO_4$ in KOH) and titrating the ammonia formed. The thorium and scandium compounds were dissolved in toluene and then extracted with aqueous NaF–HF. The precipitated fluorides were then ignited to their respective oxides. The zirconium and hafnium compounds were fused with Na_2CO_3 and pyrosulphate, precipitated with NH_4OH and subsequently ignited to the oxides. The uranyl and cerium compounds were dissolved in HCl and HNO_3 and fumed to destroy the carbon. The solution was then passed through Dowex-50 cation exchanger, eluted and the cations analysed by standard procedure.

Absorption measurements

The infra-red spectra were obtained by means of a Perkin–Elmer infra-red spectrophotometer, Model 21, using a sodium chloride prism. Spectra were obtained either for liquid films, KBr disks, Nujol mulls or solvent-dissolved material. Spectra of samples obtained by the potassium bromide disk method[10] were checked in Nujol mulls.

DISCUSSION AND RESULTS

The bis-(2-ethylhexyl)-phosphates of Li(I), Na(I), K(I), $Co(en)_3$(III) and $Co(NH_3)_6$(III) have been prepared. The latter two salts are of interest in that the central metal has its co-ordination number satisfied by co-ordination to ethylenediamine or ammonia. These complex cations must, therefore, have an ionic link to the phosphate.

[7] C. J. Barton, *Analyt. Chem.* **20**, 1068 (1948).
[8] J. J. Lingane, *Analyt. Chem.* **16**, 329 (1944).
[9] J. M. Pappenhagen, *Analyt. Chem.* **30**, 282 (1958).
[10] M. M. Stimson and J. J. O'Donnell, *J. Amer. Chem. Soc.* **74**, 1805 (1952).

All the salts have a limited solubility in toluene and as a result are prepared by extraction into di-*n*-butyl ether. The salts are non-crystalline, waxy solids, excepting $[Co(en)_3](DEHP)_3$ which was obtained only as an oil. The Li(I), Na(I) and K(I) salts are extracted into the ether phase with varying amounts of water, as high as 8–10 moles of water per cation being extracted. Each of the cobalt salts extracts as an anhydrous entity.

The bis-(2-ethylhexyl)-phosphates of scandium, uranyl, hafnium, zirconium and thorium were prepared from an aqueous chloride solution by extraction into a HDEHP-toluene phase. The scandium and uranyl compounds can also be obtained by extraction of their aqueous nitrate solutions. The substances obtained after solvent evaporation were anhydrous waxy solids and had a solvent/cation ratio equal to the charge of the cation. The species extracting into the organic phase were anhydrous. On the basis of the analytical data obtained for the solids isolated in the saturated organic phase an equilibrium (1) such as

$$M^{4+}_{(aq)} + 2H_2Y_{2(org)} \rightleftharpoons MY_{4(org)} + 4H^{+}_{(aq)} \quad (1)$$

can be postulated where H_2Y_2 represents the $(HDEHP)_2$ dimer. This is analogous to the equilibrium found for tetravalent metal extractions into TTA (i.e. thenoyl trifluoroacetone) from $HClO_4$ solutions. However, in view of the complex nature of the aqueous solutions of the polyvalent cations the data are also consistent with the equilibrium (2) in neutral aqueous chloride solutions.

$$M^{4+}_{(aq)} + 2HOH + 2H_2Y_{2(org)} \rightleftharpoons M(OH)_2(HY_2)_{2(org)} + 4H^{+}_{(aq)} \quad (2)$$

In addition more complex equilibria involving polynuclear cation species are possible, and are not ruled out by our data. The product MY_4 from equilibrium (1) cannot be distinguished from the species $M(OH)_2(HY_2)_2$ or $MO(HY_2)_2$ or $MO(HY)_2Y_2$ on the basis of solvent/cation ratios. Thus, some of the extracting species extracting from aqueous chloride solution can possibly be oxygenated. Radioactive tracer studies[11] with ^{230}Th, to be reported in detail elsewhere, have shown that the extraction of tracer-level Th(IV) is approximately third-power dependent on the HDEHP concentration in the organic phase and inverse fourth-power dependent on the mineral acid concentration in the aqueous phase, where the mineral acid is HCl or $HClO_4$. These tentative dependencies are consistent with either or both of the following equilibria (3) and (4)

$$M^{4+}_{(aq)} + 3H_2Y_{2(org)} \rightleftharpoons MY_2(HY_2)_{2(org)} + 4H^{+}_{(aq)} \quad (3)$$

$$M^{4+}_{(aq)} + HOH + 3H_2Y_{2(org)} \rightleftharpoons M(OH)(HY_2)_{3(org)} + 4H^{+}_{(aq)} \quad (4)$$

It should be noted that these data pertain to systems in which the HDEHP is present in large excess, as opposed to the saturation data reported here.

Extraction into an HDEHP–toluene phase from an aqueous nitrate solution of Ce(IV), Th(IV), Hf(IV), and Zr(IV) (Table 1) gave a saturated organic phase containing essentially one nitrate per metal atom. In the case of Ce(IV) and Zr(IV) only about two $DEHP^-$ entities per metal atom were found. It is thus postulated that the extracted

[11] D. F. PEPPARD, Unpublished data.

metal atom is oxygenated (either oxygen or hydroxyl) and that the equilibrium can be presented as (5):

$$M^{4+}_{(aq)} + HOH + NO^{-}_{3(aq)} + H_2Y_{2(org)} \rightleftharpoons M(NO_3)OH(Y)_{2(org)} + 3H^{+}_{(aq)} \quad (5)$$

In view of the fact that the infra-red spectra of these mixed nitrate-phosphates of the tetravalent cations fail to show an OH band the oxygenated complexes are more probably oxy complexes and can be represented as $[MO_{0\cdot5}NO_3(DEHP)_2]_n$. With Hf(IV) and Th(IV) the extraction from a neutral nitrate solution gave $DEHP^-/M^{4+}$ ratios of three and NO_3^-/M^{+4} ratios of one. Here, in addition to (5), equilibria of the type

$$M^{4+}_{(aq)} + NO^{-}_{3(aq)} + 1\cdot5\, H_2Y_{2(aq)} \rightleftharpoons M(NO_3)Y_{3(org)} + 3H^{+}_{(aq)}$$

as well as others, must be considered.

It has been generally assumed that hydrolysed metallic species do not extract appreciably into an organic phase. However, in addition to the results presented in this paper, there is evidence from tracer studies[11] with Zr(IV), Bi(III), Pb(II) and Pa(V) in HDEHP indicating that some of the extracting species are oxygenated (either oxygen or hydroxyl). It is also quite possible that these oxygenated species are polymerized through the oxygen, which may act as a bridge. In this connexion it should be noted that BAES *et al.*[4] have explained their results of the extraction of U(VI) into HDEHP in terms of $UO_2(DEHP)_2$ polymerization. Examples of the olation reaction with Ce(IV),[12–14] Zr(IV),[15–18] Hf(IV)[19] and Th(IV)[20,21] are well known. To test the postulate that these compounds are polymeric, molecular weight determinations using the isopiestic method are being made. The results of preliminary isopiestic studies are consistent with the proposed structure for the polymeric uranium (VI)–HDEHP complex of BAES *et al.*[4] Molecular aggregates containing a minimum of three metal atoms have been obtained.

The range of data presented for the zirconium extraction in Table 1 are those obtained from the analyses of several samples. It is conceivable that the variation could occur over a larger range. In addition, it is quite probable that in the extraction of the oxygenated species several species are involved with varying formal ratios, and also with varying states of polymerization. The higher formal ratio NO_3^-/M^{4+} for Zr(IV), Table 1, was obtained for a non-washed organic extract; the lower NO_3^-/M^{4+} ratio was obtained for a water-washed organic extract. It is noted that the water washing varies the nitrate ratio by a factor of two with only a slight variation of the $DEHP^-/M^{4+}$ ratio for Zr(IV). Th(IV), having a slighter tendency toward hydrolysis than Zr(IV), shows only a slight change in these ratios when the organic extract is washed.

[11] M. S. SHERRILL, C. B. KING and R. C. SPOONER, *J. Amer. Chem. Soc.* **65**, 170 (1953).
[12] E. L. KING, and M. L. PANDOW, *J. Amer. Chem. Soc.* **74**, 1966 (1952).
[14] B. D. BLAUSTEIN and J. W. GRYDER, *J. Amer. Chem. Soc.* **79**, 540 (1957).
[15] B. A. J. LISTER and L. A. MCDONALD, *J. Chem. Soc.* 4315 (1952).
[16] R. E. CONNICK and W. H. MCVEY, *J. Amer. Chem. Soc.* **71**, 3182 (1949).
[17] A. J. ZIELEN and R. E. CONNICK, *J. Amer. Chem. Soc.* **78**, 5785 (1956); A. J. ZIELEN, U.S.A.E.C. Report UCRL–2268. July, 1953.
[18] K. A. KRAUS and J. S. JOHNSON, *J. Amer. Chem. Soc.* **75**, 5769 (1953).
[19] J. S. JOHNSON and K. A. KRAUS, *J. Amer. Chem. Soc.* **78**, 3937 (1956); J. S. JOHNSON, K. A. KRAUS and R. W. HOLMBERG, *Ibid.* **78**, 26 (1956).
[20] E. L. ZEBROSKI, W. H. ALTER and F. K. HEUMANN, *J. Amer. Chem. Soc.* **73**, 5646 (1951).
[21] S. HIETANEN, *Rec. Trav. Chim.* **75**, 712 (1956); *Acta Chem. Scand.* **8**, 1626 (1954).

TABLE 1.—ANALYTICAL RESULTS OF VARIOUS NITRATE-BIS-(2-ETHYLHEXYL)-PHOSPHATES

Cation	$DEHP^-/M^{4+}$	Organic phase NO_3^-/M^{4+}	H_2O	Postulated complex in saturated organic phase
Hf(IV)	3·1	1·2	nil	$Hf(NO_3)(DEHP)_3$
Zr(IV)	1·8–2·2	0·6–1·2	nil	$[ZrO_{0\cdot5}(NO_3)(DEHP)_2]_n$
Ce(IV)	2·1	1·0	nil	$[CeO_{0\cdot5}(NO_3)(DEHP)_2]_n$
Th(IV)	2·8	1·1	nil	$Th(NO_3)(DEHP)_3$

TABLE 2.—OBSERVED FREQUENCIES AND ASSIGNMENTS FOR TRIS-(2-ETHYLHEXYL)-PHOSPHATE AND BIS-(2-ETHYLHEXYL)-PHOSPHORIC ACID

Tris-(2-ethylhexyl)-phosphate	Postulated assignments	Bis-(2-ethylhexyl)-phosphoric acid
	Methyl, methylene	
2960 (vs) broad	C—H stretching	2965 (vs) broad
2890 (sh)	(sym. & antisym.)	2930 (sh)
		2870 (sh)
	O—H (st.) bonded	2750–2550 (s) broad
		2280 (s) broad
	O—H deformation	1680 (m) broad
1470 (m)	CH_3 deg. deformation CH_2 scissor	1470 (m)
1385 (w)	CH_3 sym. deformation	1385 (w)
1283 (s)	←P→O st. (doublet)	
1267		
	P→O stretching ⟶	1225 (s)
1155 (w)	C—C—C antisym. st.	1155 (m)
1115 (w)	C—O stretching (antisym.)	1115 (w)
1025 (vs) broad	P—O st. (antisym.)	1040 (vs) broad
885 (m)	CH_2 wagging	885 (m)
840 (w)		
788 (w)		780 (w)
745 (w)	P—O st. (sym.)	720 (w)

Abbreviations: (w) weak; (m) medium; (s) strong; (v) very; (sh) shoulder.

Infra-red absorption measurements

(A) *Tris-(2-ethylhexyl)-phosphate* and bis-(2-ethylhexyl)-phosphoric acid.* The observed frequencies for TEHP and HDEHP are listed in Table 2. The assignment of the frequencies for the organic portion in these molecules was made by comparison with the spectrum of 3-(chloromethyl)-heptane. The assignment of the frequencies of the phosphorus portion in these molecules was made by comparison with the spectra of other tertiary and secondary phosphates.

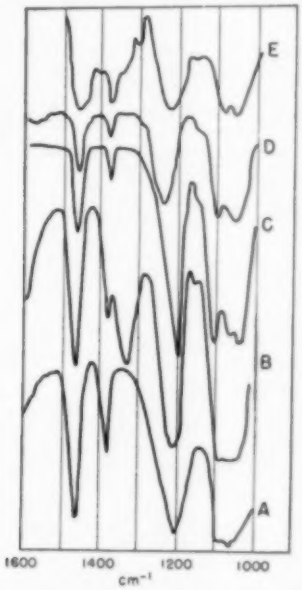

FIG. 1.—Infra-red absorption of the bis-(2-ethylhexyl)-phosphate salts of $Co(en)_3$(III), $Co(NH_3)_6$(III), Li(I), Na(I) and K(I).

It is observed that the P → O band for TEHP is a doublet and occurs at 1283 and 1267 cm^{-1}. MORTIMER[22] has discussed the P → O doublet in tertiary phosphates as being due to rotational isomerism.

The associated nature of the hydroxyl and P → O groups in HDEHP have been discussed previously.[5,6] The HDEHP dimerization presumably occurs through formation of an eight-membered ring by means of hydrogen bonding. The bonded OH vibration occurs in a broad region of 2550–2750 cm^{-1}. The hydrogen bonding is of a more stable nature than that in monocarboxylic acids.[6,23] Dilutions in CCl_4 fail to produce a free OH band. The P → O band in HDEHP is that of a bonded P → O and occurs at 1225 cm^{-1}, and does not change with dilution.

(B) *Salts of bis-(2-ethylhexyl)-phosphoric acid.* The infra-red spectra of the Li(I), Na(I), K(I), $Co(en)_3$(III) and $Co(NH_3)_6$(III) salts of HDEHP in the region 1000–1500 cm^{-1} are illustrated in Fig. 1. The observed infra-red frequencies are listed in Table 3. For comparative purposes there are also listed the observed frequencies of $[Co(en)_3]Cl_3$ and $[Co(NH_3)_6]Cl_3$.

* Abbreviated henceforth as TEHP.

[22] F. S. MORTIMER, *Spectrochim. Acta* **9**, 270 (1957).

[23] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).

The unbonded P → O frequency at about 1250–1300 cm^{-1}, in tertiary phosphates is comparable to the C=O frequency observed in monocarboxylic esters at 1750 cm^{-1}. These are the unbonded phosphoryl and carbonyl frequencies, respectively, in covalent compounds. Salt formation with the monocarboxylic acids gives an antisymmetric carboxylate ion frequency at 1600–1650 cm^{-1}. Salt formation with HDEHP gives an antisymmetric POO^- stretching frequency at about 1200 cm^{-1}. This agrees with the results for this vibration of MAARSEN,[24] for the salts of several alkyl phosphoric acids, and with those of BELLAMY[25] for several silver and lead salts of organophosphoric

TABLE 3.—ABSORPTION MAXIMA IN cm^{-1} OF THE BIS-(2-ETHYLHEXYL)-PHOSPHATE SALTS OF Li(I), Na(I), K(I), $Co(en)_3$(III) AND $Co(NH_3)_6$(III) [KBr DISK SPECTRA]; $[Co(NH_3)_6]Cl_3$ AND $[Co(en)_3]Cl_3$ [KBr DISK SPECTRA]

Li[DEHP]	Na[DEHP]	K[DEHP]	$[Co(NH_3)_6]$ $[DEHP]_3$	$[Co(NH_3)_6]Cl_3$	$[Co(en)_3]$ $[DEHP]_3$	$[Co(en)_3]Cl_3$
3400 (w)	3425 (m)	3475–2825 (vs) broad	3160 (s) broad	3210–3003 (s) broad	3110–2827 (vs) broad	3470 (m)
2944 (s)	2924 (s)		2939 (s)			3100–3003 (s) broad
2877 (sh)	2877 (sh)		2877 (sh)			2350 (m)
			1620 (m)	1600 (m)	1610 (w)	1570 (s)
1465 (m)	1470 (m)	1466 (m)	1470 (m)		1470 (m)	1475 (m)
1385 (w)	1385 (w)	1386 (m)	1385 (w)	1328 (s)	1380 (w)	1375 (m)
		1321 (w)	1328 (m)			1330 (m)
1196 (vs)	1243 (vs)	1238 (vs)	1205 (vs)		1203 (vs)	1280 (m)
						1250 (m)
						1150 (m)
						1128 (m)
1102 (vs)	1100 (vs)	1098 (vs)	1092 (vs)		1093 (vs)	
1035 (vs)	1053 (vs)	1060 (vs)	1048 (vs)		1050 (vs)	1050 (m)
						1000 (sh)
					930 (w)	900 (w)
885 (s)	860 (m)	870 (m)	860 (m)	825 (m)		
		820 (m)			870 (m)	830 (m)
		780 (w)				
		730 (w)				

Abbreviations: (w) weak; (m) medium; (s) strong; (v) very; (sh) shoulder.

acids. The spectra of the salts of HDEHP are comparatively simple. The broad bonded OH band present in HDEHP at 2550–2750 cm^{-1} is absent in these salts, as is to be expected. The antisymmetric POO^- stretching vibration in the Li(I) salt appears at 1196 cm^{-1}; that of the $Co(en)_3$(III) salt at 1203 cm^{-1}; and that of the $Co(NH_3)_6$(III) salt at 1205 cm^{-1}. This vibration appears as a very strong band in all these compounds. These spectra were obtained in the solid state (KBr disks) and checked in Nujol mulls. Results in dibutyl ether for these salts are similar. The Na(I) and K(I) salts are different in their behaviour for they seem to show a solid or lattice effect, which shifts the antisymmetric POO^- stretching vibration to a higher frequency. In the solid state the antisymmetric POO^- vibration occurs at 1243 cm^{-1} for the Na(I) salt and at 1238 cm^{-1} for the K(I) salt (KBr disks and Nujol mulls), while for the Na(I) salt in dibutyl ether this band is at 1203 cm^{-1}, and for the K(I) salt in the liquid film spectrum it is at 1204 cm^{-1}. These shifts can also be explained in terms of a greater degree of covalency in the metal to oxygen bond of the phosphate in the solid state than in solution. MAARSEN[24] has shown that in the sodium and potassium salts of

[24] J. W. MAARSEN and M. C. SMIT, *Rec. Trav. Chim.* **76**, 724 (1957).
[25] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, New York (1954).

dimethyl, diethyl and di*iso*propyl phosphates the POO^- antisymmetrical frequency appears at about 1240–1250 cm^{-1} in the solid state. Table 4 shows the comparison of the observed antisymmetric POO^- absorption for these salts in the solid state and in solution.

With the Li(I), Na(I), K(I), $Co(en)_3$(III) and $Co(NH_3)_6$(III) salts it was also observed that another strong absorption occurs at 1100 cm^{-1}, although this is somewhat masked since it occurs in a region where several vibrations are taking place. It is suggested that this is the POO^- symmetrical stretching vibration and agrees with the

TABLE 4.—COMPARISON OF THE ANTISYMMETRIC POO^- BAND IN SOLID SPECTRA AND SOLVENT SPECTRA FOR VARIOUS SALTS OF HDEHP

Salt	Frequency of POO^- antisymmetric band (cm^{-1})		
	KBr* disk spectra	Di-(*n*-butyl) ether solution spectra	CCl_4 solution spectra
Li[DEHP]	1196	1208	1201
Na[DEHP]	1243	1203	—
K[DEHP]†	1238	—	—
$[Co(en)_3][DEHP]_3$	1203	1195	—
$[Co(NH_3)_6][DEHP]_3$	1205	1195	—

* Results the same as those obtained in Nujol mulls.
† Liquid film spectra show the POO^- vibration occurring at 1204 cm^{-1}.

position of about 1080 cm^{-1} assigned to this bond by others.[26,27] The region of 1000–1100 cm^{-1} then is probably an overlapping of the POO^- symmetrical stretching absorption, C—O antisymmetrical stretching absorption and the P—O antisymmetrical stretching absorption.

(C) *Bis-(2-ethylhexyl)-phosphates of* Sc(III), Zr(IV), Hf(IV), Th(IV) *and* U(VI). The bis-(2-ethylhexyl)-phosphates of Sc(III), Zr(IV), Hf(IV), Th(IV) and U(VI) have been prepared, and the infra-red spectra are shown in Fig. 2. The observed infra-red frequencies are listed in Table 5.

The broad bonded OH region at 2550–2750 cm^{-1} present in HDEHP has disappeared. With the exceptions of the Sc(III) and Th(IV) compounds the region of 1100–1250 cm^{-1} is more complex than that observed in the salts of HDEHP. The Sc(III) compound has a strong absorption at 1201 cm^{-1} and a weaker absorption at 1104 cm^{-1} and these are presumably the POO^- antisymmetric and symmetric frequencies respectively. This spectrum bears a strong resemblance to that observed with the salts of HDEHP, and the scandium-to-oxygen bond in the phosphate may have a high ionic character. The spectrum of the Th(IV) compound appears to be similar to that of Sc(III). It has a strong doublet at 1193 cm^{-1} and 1160 cm^{-1}, and a very intense band at about 1100 cm^{-1}. The spectra of the Hf(IV) and Zr(IV) compounds are very similar to each other and somewhat different from those of Sc(III) and Th(IV). A strong broad POO^- antisymmetric band is observed at 1250 cm^{-1} with medium bands at about 1200 cm^{-1}. Another broad peak is observed at 1050 cm^{-1} with a shoulder at 1100 cm^{-1}. Both the Hf(IV) and Zr(IV) compounds of HDEHP show a

[26] H. GERDING and J. W. MAARSEN, *Rec. Trav. Chim.* **76**, 431 (1957).
[27] D. E. C. CORBRIDGE and E. J. LOWE, *J. Chem. Soc.* 4555 (1954).

shifted antisymmetric POO^- frequency to about 1250 cm^{-1} (Table 6), which is intermediate between that of TEHP and of the salts of HDEHP. With hafnium, this shift takes place in the KBr disk, Nujol mull, liquid film and toluene solution spectra. With zirconium, the shift occurs only in the solid state. For the liquid film and toluene

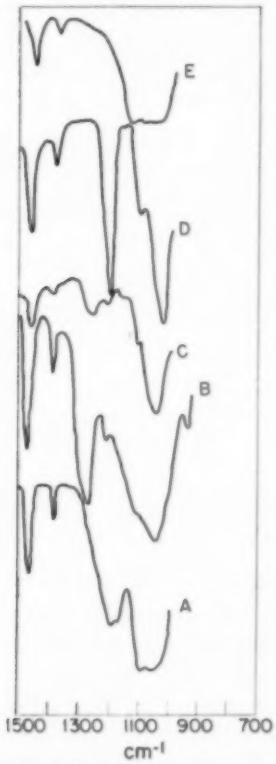

FIG. 2.—Infra-red absorption spectra of bis-(2-ethylhexyl)-phosphates of Sc(III), Hf(IV),Th(IV), Zr(IV) and U(VI).

solution spectra, it is back to about 1206 cm^{-1}. The shift may be interpreted as an indication that the zirconium bond to the oxygen in the phosphate in the solid state is of a more strongly covalent character than is the corresponding bond of the Sc(III) or Th(IV) compounds. For hafnium, the bonding is definitely more covalent, since all spectra showed this shifted POO^- frequency. This interpretation is similar to that made in studies of the following complexes: oxalato–metal,[28] glycino–metal,[29] alanino–metal[30] and prolino–metal[31] by the group at the University of Notre Dame.

(D) *The mixed nitrate and bis-(2-ethylhexyl)-phosphate complexes of* Ce(IV), Th(IV),

[28] M. J. SCHMELZ, T. MIYAZAWA, S. MIZUSHIMA, T. J. LANE and J. V. QUAGLIANO; *Spectrochim. Acta* **9**, 51 (1957).
[29] A. J. SARACENO, I. NAKAGAWA, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer.Chem. Soc.* **80**, 5018 (1958).
[30] D. SEGNINI, C. CURRAN, K. FUKUSHIMA, S. MIZUSHIMA and J. V. QUAGLIANO, Paper presented at Amer. Chem. Soc. 133rd meeting, San Francisco, California, April 13–18 (1958).
[31] D. SEGNINI, J. V. QUAGLIANO and C. CURRAN, Paper presented at Amer. Chem. Soc., 134th Meeting, Chicago, Illinois, September 7–12, (1958).

Zr(IV) *and* Hf(IV). Extractions into HDEHP of neutral aqueous Ce(IV), Th(IV), Zr(IV) and Hf(IV) nitrate solutions give saturated organic phases which contain nitrate in a ratio of one mole of nitrate to one atom of metal. Analyses of the organic solutions of Th(IV) and Hf(IV) showed the phosphate-to-metal ratio to be 3 : 1. Thus the

TABLE 5.—ABSORPTION MAXIMA IN cm^{-1} OF THE COMPLEXES OF Th(IV), Zr(IV), Hf(IV), Sc(III) AND UO_2(II) WITH BIS-(2-ETHYLHEXYL)-PHOSPHORIC ACID [KBr DISK SPECTRA]

$Th[DEHP]_4$	$Zr[DEHP]_4$	$Hf[DEHP]_4$	$Sc[DEHP]_3$	$UO_2[DEHP]_2$
2939 (s)	2924 (s) broad	2914 (s) broad	2929 (s)	2914 (s) broad
2877 (sh)	2872 (sh)		2877 (sh)	
	1460 (m)	1460 (m)	1468 (w)	1465 (m)
	1377 (w)	1380 (w)	1385 (w)	1380 (w)
1193 (s)	1250 (s)	1250 (s)		
1160 (sh)	1205 (sh)	1200 (m)	1201 (s)	1130 (s)
	1150 (w)			
1090 (vs)	1100 (sh)	1100 (sh)	1104 (w)	
1057 (vs) broad	1050 (vs) broad	1040 (vs) broad	1030 (vs) broad	1065 (vs) broad
890 (s)	890 (s)	920 (m)	900 (w)	930 (m)
				880 (w)
770 (w)	780 (m)		770 (w)	810 (w)
730 (m)				770 (w)

Abbreviations: (w) weak; (m) medium; (s) strong; (v) very; (sh) shoulder.

complexes in these solutions are postulated as $ThNO_3[DEHP]_3$ and $HfNO_3[DEHP]_3$ The analyses of the organic solutions of Ce(IV) and Zr(IV) showed the phosphate-to-cation ratio to be 2 : 1. Therefore, to balance charges, a mole of hydroxyl or 0·5 mole of oxygen per atom of metal is postulated.

TABLE 6.—COMPARISON OF THE ANTISYMMETRIC POO^- BAND FOR $Zr[DEHP]_4$ AND $Hf[DEHP]_4$ COMPLEXES IN VARIOUS STATES

Compound	KBr Disk	Frequency of POO^- antisymmetric band (cm^{-1})		
		Nujol mull	Liquid film	Toluene solution
$Zr[DEHP]_4$	1250 (s)	1250 (s)	1248 (sh)	1245 (sh)
	1205 (sh)	1210 (m)	1206 (s)	1204 (s)
$Hf[DEHP]_4$	1250 (s)	1250 (s)	1260 (s)	1256 (vs)
	1220 (sh)	1218 (m)	1211 (m)	1206 (s)

Fig. 3 depicts the spectra and Table 7 shows the observed frequencies for these mixed nitrate–phosphate complexes. The broad OH bonded region at 2550–2750 cm^{-1}, which is present in HDEHP, has disappeared. In addition, there appears no free OH band in any of these mixed complexes, and therefore the complexes of Ce(IV) and Zr(IV) are probably bonded to oxygen rather than to a hydroxyl group.

The nitrate vibrations in these mixed complexes are characteristic of a nitrate group co-ordinated to a metal atom. GATEHOUSE *et al.*[32] recently studied the spectra of several nitrato-complexes of metals and made assignments for vibrations characteristic of co-ordinated nitrato-groups. They listed the region of 1480–1530 cm^{-1} as the NO_2 antisymmetric stretching vibration; the region of 1250–1290 cm^{-1} as the NO_2 symmetric stretching vibration; the region of 970–1034 cm^{-1} as the O—N stretching vibration; and the region of 781–800 cm^{-1} as the nonplanar rocking vibration. Similar results[33] have been obtained for the co-ordination compound $[Co(NH_3)_5NO_3]Cl_2$. The results for all the mixed nitrate–phosphate complexes

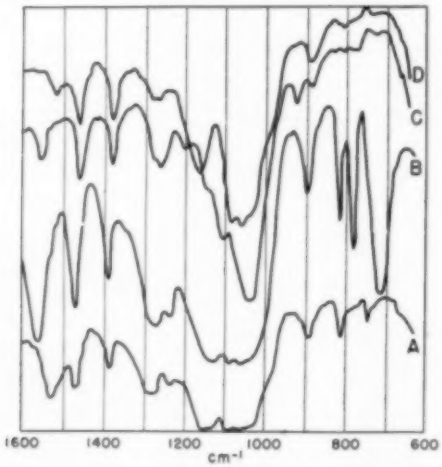

FIG. 3.—Infra-red absorption spectra of the mixed nitrate and bis-(2-ethylhexyl)-phosphates of Th(IV), Zr(IV), Hf(IV) and Ce(IV).

reported in this paper show the NO_2 antisymmetric stretching vibration in the region 1520–1565 cm^{-1}; the NO_2 symmetric stretching vibration in the region of 1265–1285 cm^{-1}. The O—N stretching band at 1017 cm^{-1} is masked in these compounds by the strong, broad band at 1000–1100 cm^{-1}. Both the Th(IV) and Zr(IV) also show the nonplanar rocking vibration of the co-ordinated nitrato group at about 820 cm^{-1}. The Ce(IV) and Hf(IV) compounds do not show this band clearly, but this may be due to the low concentration of the compound in the KBr disk. The bonding of the metal atom presumably involves the oxygen of the nitrate as the donor atom, and the bonding is probably essentially covalent. Absorption bands of the NO_3^- ion are not observed.

The region of 1100–1240 cm^{-1} in these mixed nitrate-bis-(2-ethylhexyl)-phosphates is of interest. It appears to be different from that for the bis-(2-ethylhexyl)-phosphates but is similar to the spectrum in this region for the compound $UO_2[DEHP]_2$. The Th(IV), Zr(IV) and Hf(IV) compounds show a strong band at about 1200–1230 cm^{-1}, but a much stronger band appears in the vicinity of 1100–1145 cm^{-1} (1141 cm^{-1} for Th, 1120 cm^{-1} for Zr, and 1110 cm^{-1} for Hf). The Ce(IV) compound shows a strong

[32] B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM, *J. Chem. Soc.* 4222 (1957).
[33] J. V. QUAGLIANO, Private Communication and paper presented at Amer. Chem. Soc., 132nd Meeting, Miami, Florida, April 7–12, (1957).

band at 1158 cm^{-1} and fails to show anything in the 1200–1230 cm^{-1} region. It is believed that the phosphate is probably bonded to the metal in these mixed compounds differently than it is in the pure phosphate compounds. The shift can be explained if the bonding is of a covalent nature to both oxygens of the POO^- group, and this gives single bond character to both P—O bonds. There is then a shift towards lower frequency toward the vicinity of a P—O vibration (1000–1100 cm^{-1} for the P—O vibration). An alternative explanation is that these shifts are due to the polymeric nature of these substances. The polymeric nature of these compounds has already been demonstrated by isopiestic techniques.

TABLE 7.—ABSORPTION MAXIMA IN cm^{-1} OF THE NITRATE-BIS-(2-ETHYLHEXYL)-PHOSPHATES OF Th(IV), Zr(IV), Hf(IV) AND Ce(IV) [KBr DISK SPECTRA]

$Th(NO_3)[DEHP]_3$	$[ZrO_{0.5}(NO_3)(DEHP)_2]_n$	$Hf(NO_3)(DEHP)_3$	$[CeO_{0.5}(NO_3)(DEHP)_2]_n$
2944 (s)	2934 (s)	2934 (s)	2937 (s)
2882 (sh)	2877 (sh)	2867 (sh)	2878 (sh)
1532 (s)	1553 (s)	1565 (s)	1520 (w)
1476 (s)	1462 (s)	1463 (s)	1460 (m)
1386 (m)	1386 (s)	1383 (s)	1378 (w)
1278 (s)	1270 (s)	1285 (s)	1265 (w)
1233 (s)	1230 (s)	1205 (s)	
		1145 (sh)	
1141 (vs)	1120 (vs)	1110 (vs)	1158 (s)
1090 (vs)	1090 (vs)		1080 (vs)
1060 (vs) broad	1060 (vs) broad	1040 (vs) broad	1050 (vs)
		925 (w)	
890 (w)	895 (w)	885 (w)	880 (w)
		830 (w)	
810 (w)	810 (w)	810 (w)	810 (w)
743 (w)	780 (m)	785 (w)	740 (w)
	710 (s)	725 (w)	

Abbreviations: (w) weak; (m) medium; (s) strong; (v) very; (sh) shoulder.

The formation of mixed nitrate-bis-(2-ethylhexyl)-phosphates with the tetravalent cations, when extraction from aqueous nitrate solutions is made, is somewhat surprising. Extraction from aqueous chloride solutions gives the expected bis-(2-ethylhexyl)-phosphates. In addition Sc(III) and U(VI) give the normal phosphates in extractions from both nitrate and chloride solutions. Thus, although nitrates are considered to be poor complexing substances, and fail to complex Th appreciably in the aqueous phase, nitrate complexing of Th(IV) (and perhaps M(IV) in general) into very stable complexes does occur in the organic phase. The difficulty encountered in determining the nitrates analytically lends further support to the extreme stability of the mixed nitrate-phosphate complexes. Agitation of one formula weight of the mixed thorium nitrate–phosphate complex $[Th(NO_3)(DEHP)_3]$ and one formula weight of HDEHP with a series of water washes fails to remove the nitrate, as evidenced by the infra-red spectra. In addition, upon agitation of a saturated toluene solution of the $Th(DEHP)_4$ compound with an excess of an aqueous solution of $Th(NO_3)_4$, additional thorium

is extracted into the organic phase, and the spectrum becomes that of the $Th(NO_3)(DEHP)_3$ compound.

The isopiestic studies of these compounds will be extended. The present study will also be extended to include extractions of other inorganic anions and extractions from mineral acid media.

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THE CHEMISTRY OF PROTACTINIUM—V

A COMPARISON OF THE EXTRACTION OF PROTACTINIUM, NIOBIUM AND TANTALUM

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Abstract—A quantitative comparison has been made of the extraction of niobium, tantalum and protactinium from solution in hydrochloric acid by di-*iso*propylcarbinol. The effects of acid, hydrogen ion and chloride ion concentrations are reported, as well as the effect of the addition of fluoride ions. Similar data on the extraction of protactinium from bromide, sulphate and oxalate solutions are included.

The results are discussed in terms of the theories of solvent extraction of IRVING and ROSOTTI and of DIAMOND and complex ions of protactinium that might account for the results are suggested.

Two previous papers in this series have dealt with the solvent extraction of protactinium.[1,2] The first deals principally with the conditions for extraction and the second the choice of organic solvent. In this paper the intention is to compare the behaviour of the element with those of niobium and of tantalum under the same conditions.

Although the extraction of these elements from solutions in mixtures of hydrochloric and hydrofluoric acids has been studied in some detail,[3–7] and although it has been known for a long time that ethers, alchohols and ketones extract at least traces of these elements from solutions in hydrochloric acid,[8] the latter process has not received much attention. HICKS and GILBERT showed that niobium was extracted much more readily by di-*iso*propyl ketone from hydrochloric acid solution than by tantalum.[9] Again, separation of niobium from tantalum has been reported by extraction from similar solutions using a solution of trioctylamine in xylene.[10,11] Protactinium can also be extracted by both these reagents[10,12] and studies in this laboratory suggest a close analogy between protactinium and niobium. A more detailed comparison of the three elements seemed profitable since it might facilitate identification of the complex ions in the protactinium solutions.

Unfortunately di-*iso*propyl ketone, the solvent for which the most detailed information on the behaviour of protactinium was already available, had become commercially unavailable, and another solvent was chosen for the comparison. Earlier

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[1] A. G GOBLE, J. GOLDEN and A. G. MADDOCK, *Canad. J. Chem.* **34**, 284 (1956).
[2] A. G. GOBLE and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **7**, 94 (1958).
[3] G. A. WOOD, UKAEA Document CRL/AE 62 (1950).
[4] F. H. BURSTALL, P. SWAIN, A. F. WILLIAMS and G. A. WOOD, *J. Chem. Soc.* 1497 (1952).
[5] H. G. HICKS and G. STEVENSON, *Analyt. Chem.* **25**, 1517 (1953).
[6] J. R. WERNING and K. B. HIGBIC, *Industr. Engng. Chem.* **46**, 2491 (1954).
[7] J. M. FLETCHER, D. F. C. MORRIS and A. G. WAIN, *Trans. Inst. Mining Met.* **65**, 487 (1955).
[8] G. H. MORRISON, *Analyt. Chem.* **22**, 1388 (1950).
[9] H. G. HICKS and R. S. GILBERT, *Analyt. Chem.* **26**, 1205 (1954).
[10] G. W. LEDDICOTTE and F. L. MOORE, *J. Amer. Chem. Soc.* **74**, 1618 (1952).
[11] J. Y. ELLENBERG, G. W. LEDDICOTTE and F. L. MOORE, *Analyt. Chem.* **26**, 1045 (1954).
[12] F. L. MOORE, *Analyt. Chem.* **27**, 70 (1955).

work has shown that di-*iso*propyl carbinol is suitable for all three extractions and it was selected for the present study. However, before investigations were complete it again became necessary to synthesize the solvent because of failure of commercial supplies.

In the earlier investigations of these extractions, plots of the logarithm of the extraction coefficient against the logarithm of the activity of the hydrochloric acid in the aqueous phase were found to be much more closely linear than might be expected.[1,2] An attempt has therefore been made to increase the precision of the measurements so that closer limits to the deviations from linearity might be established.

EXPERIMENTAL

Commercial "ANALAR" acids and salts were used in these experiments; no further purification was found necessary. When the commercial supply of di-*iso*propyl carbinol ceased it was prepared (a) by the reduction of di-*iso*propyl ketone by lithium aluminium hydride and (b) by a Grignard reaction using *iso*propyl bromide and *iso*butyraldehyde.[13] Both products behaved in the same way.

Tracer concentrations of the metals were used in all experiments. Concentrated stock solutions were prepared and appropriate aliquots added to the aqueous phase shortly before equilibrium with the solvent. ^{233}Pa stock in hydrochloric acid was prepared from neutron irradiated thorium nitrate as described previously.[2] ^{182}Ta was obtained in the form of irradiated tantalum pentoxide. The oxide was fused with sodium carbonate and the melt leached with warm water. The hydrated oxide was precipitated from this solution and dissolved in ammonium oxalate solution. ^{95}Nb was obtained from the Radiochemical Centre in an oxalic acid solution and used as received. The absence of colloidal materials in the various solutions was periodically verified by repartitioning the separated phases with the opposite phases, free from tracer, and observing that all three extraction coefficients had the same value. The concentrations of the protactinium trace solutions were in the range 10^{-10}–10^{-11} M. The niobium and tantalum tracers were approximately 10^{-4}–10^{-5} M.

The procedures for equilibration and determination of the extraction coefficient have been described previously.[2] The experiments were done in seven millilitre snap-closure polythene capsules. No ageing of the polythene vessels by the solvents was found necessary. Di-*iso*propyl carbinol is more basic than most of the solvents used previously, and a more elaborate pre-equilibration with the acid proved necessary. Even two pre-equilibrations with equal volumes of acid were insufficient at the higher concentrations of hydrochloric acid. A calibration curve was therefore constructed by titrating the equilibrium acid phase after two pre-equilibrations with equal volumes of the aqueous acid, giving the final acidity; this correction became important at 4·5 M acid. Aliquots of both phases were assayed in a standard scintillation counter in similar polythene capsules fitting the well in the crystal. Only the photoabsorption pulses were counted and no corrections were necessary for the density of the liquid. In all cases equilibration was apparently complete in 2 or 3 min; to ensure completion the capsules containing the mixtures were shaken mechanically for 10 min. Since change of temperature has only a small effect on the extraction coefficient so that the systems were not thermostatted. The laboratory temperature varied between 14° and 18°.

The results of 150 measurements showed that for extraction coefficients between 0·02 and 150 reproducibility was better than ±2 per cent, but on re-equilibration reproducibility was not quite as good. The following observations relate to protactinium.

Molarity of acid phase	3·0	3·4	3·8
First equilibration	0·493	1·30	3·26
Re-equilibration of aqueous phase (Fresh organic phase)	0·498	1·28	3·23
Re-equilibration of organic phase (Fresh aqueous phase)	0·489	1·35	3·42

As with other aqueous solutions the alcoholic extracts are metastable and hydrolyse on standing, usually with adsorption on to the walls of the container. However, this effect was never observed

[13] J. B. CONANT and A. H. BLATT, *J. Amer. Chem. Soc.* **51**, 1233 (1929).

in extracts less than one day old and quite concentrated extracts, containing ^{231}Pa at 0·01 mg/ml, have been preserved unchanged for two months, so that no appreciable inconvenience and irreproducibility ensued from this behaviour.

RESULTS

I. *Chloride complexes*

The variation of the percentage extraction coefficients with the concentration of acid in the aqueous phase shows the usual sigmoid form for both niobium and tantalum; for the former, however, 8 N hydrochloric acid is required for 90 per cent

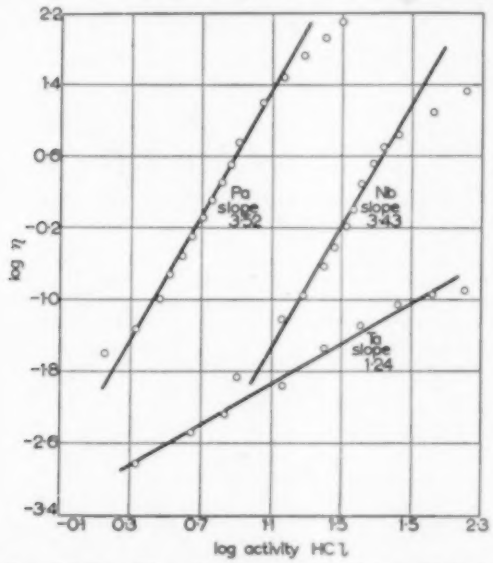

FIG. 1.—Variation of the logarithm of the extraction coefficient with the logarithm of the activity of hydrochloric acid in the aqueous phase. Data for niobium, tantalum and protactinium.

extraction, while 4 N acid suffices for the latter. On the other hand the curve for tantalum is flattened and the extraction only reaches 12 per cent at 12 N.

The variation of the extraction coefficient with the activity of the acid in the aqueous phase is shown for all three elements in Fig. 1. The activity data used are those given by RANDALL and YOUNG.[14]

The hydrogen ion dependence of the extraction coefficient of niobium and protactinium was investigated in solutions at constant total chloride concentration. Sodium chloride–hydrochloric acid mixtures were suitable for protactinium but niobium could only be studied in the solutions of higher total chloride concentration attainable with mixtures of magnesium chloride and hydrochloric acid. Fig. 2 shows the relation between the hydrogen ion concentration and the extraction coefficient for the two elements from these two solutions at constant chloride concentration.

Unfortunately activity coefficient measurements are not available for the magnesium chloride—hydrochloric acid solutions so that a plot against the logarithm of the hydrogen ion activity is only possible with the protactinium data. Such a plot gives a line of slope 1·39. Similar measurements were not practical with tantalum.

The chloride ion dependency at constant hydrogen ion concentration is shown for

[14] M. RANDALL and L. E. YOUNG, *J. Amer. Chem. Soc.* **50**, 989 (1928).

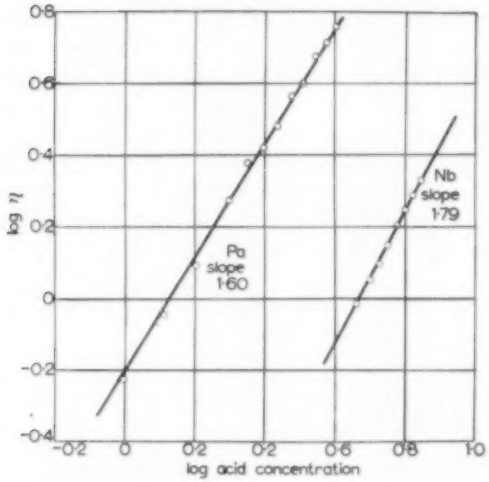

Fig. 2.—Variation of the logarithm of the extraction coefficient with the logarithm of the hydrogen ion concentration for niobium and protactinium. Niobium at a constant chloride concentration of 7 M in hydrochloric acid–magnesium chloride mixtures. Protactinium at a constant chloride concentration of 4 M in hydrochloric acid–sodium chloride mixtures.

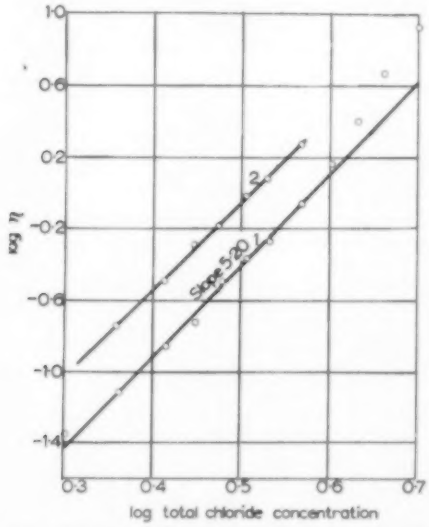

Fig. 3.—Extraction of protactinium-233 into di-*iso*propylcarbinol from aqueous HCl + NaCl solutions of varying chloride ion concentration and constant hydrogen ion concentration. Variation of the logarithm of the extraction coefficient with the logarithm of the total chloride ion concentration.
1. $(H^+) = 2$ N 2. $(H^+) = 2{\cdot}18$ N

protactinium in Fig. 3. These measurements could not be made at constant salt concentration because no inert salt has been found. Similar measurements could not be made for niobium.

II. *Fluoride complexes*

In contrast to the similarity found between niobium and protactinium in the

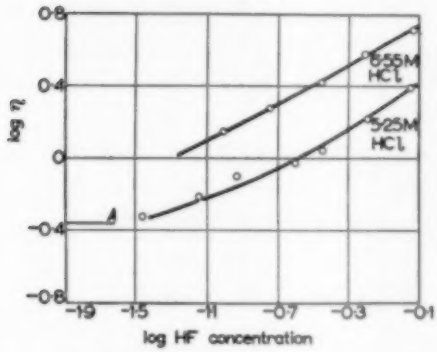

FIG. 4.—Extraction of niobium-95 into di-*iso*propylcarbinol from hydrochloric acid solutions containing varying amounts of hydrofluoric acid. Variation of the logarithm of the extraction coefficient with the logarithm of the hydrofluoric acid concentration.
(1). Hydrochloric acid concentration 5·25 M.
(2). Hydrochloric acid concentration 6·55 M.
Intercept at *A*—Extraction coefficient from 6·55 M hydrochloric acid without hydrofluoric acid.

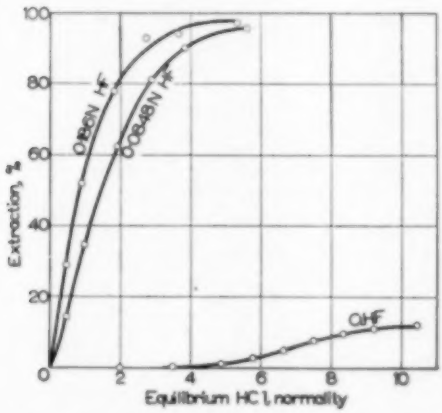

FIG. 5.—Extraction of tantalum-182 into di-*iso*propylcarbinol from hydrochloric acid solutions containing varying amounts of hydrofluoric acid. Variation of the percentage extraction with the equilibrium hydrochloric acid concentration.

chloride solutions, the addition of fluoride ions readily distinguishes these elements both from each other and from tantalum. Figs. 4 and 5 show the effect on the extraction of niobium and tantalum of small quantities of hydrofluoric acid added to the hydrochloric acid solutions. In both cases a small concentration of hydrofluoric acid causes a large increase in the extraction, the effect being most spectacular for tantalum. On the other hand hydrofluoric acid up to a concentration of 10^{-3} M may be added to a 5·77 M hydrochloric acid solution of protactinium without greatly lowering the extraction, as can be seen from Fig. 6. At higher concentrations of fluoride the extraction falls rapidly to zero and remains at this value even up to 16 M in hydrofluoric acid. The variation of the extraction coefficient for niobium with the

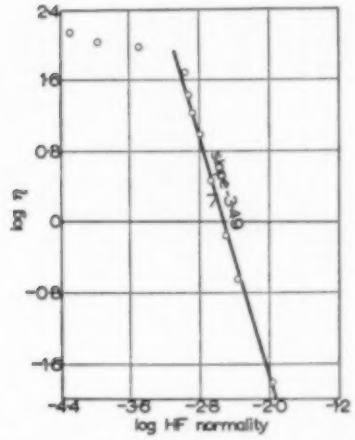

FIG. 6.—Extraction of protactinium-233 into di-*iso*propylcarbinol from 5·77 N hydrochloric acid + varying amounts of hydrofluoric acid. Variation of the logarithm of the extraction coefficient with the logarithm of the hydrofluoric acid concentration.

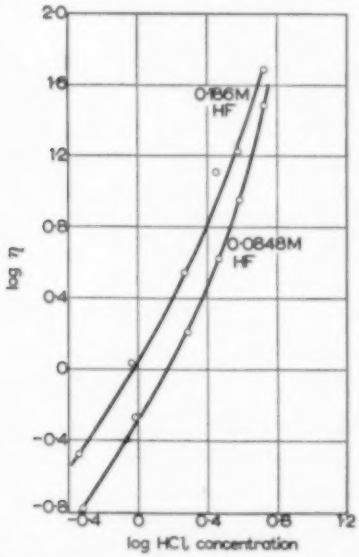

FIG. 7.—Variation of the logarithm of the extraction coefficient for niobium with the logarithm of the hydrochloric acid concentration at constant hydrofluoric acid concentration.
(1). Hydrofluoric acid concentration 0·0848 M.
(2). Hydrofluoric acid concentration 0·168 M.

concentration of hydrochloric acid at constant hydrofluoric acid concentration was investigated and the results are shown in Fig. 7.

III. *Bromide solutions*

Previous investigations[1] have shown that protactinium is less easily extracted from bromide solutions than from the chloride solutions. The variation of the extraction coefficient for protactinium with the activity of hydrobromic acid is shown in Fig. 8. The effects of hydrogen and bromide ion concentrations are shown in

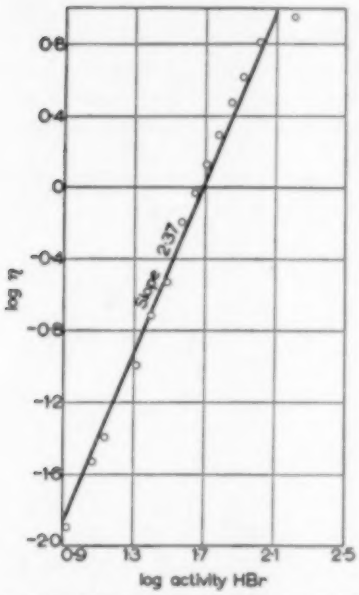

FIG. 8.—Extraction of protactinium-233 into di-*iso*propylcarbinol from hydrobromic acid solution. Variation of the logarithm of the extraction coefficient with the logarithm of the mean ionic activity of the hydrobromic acid.

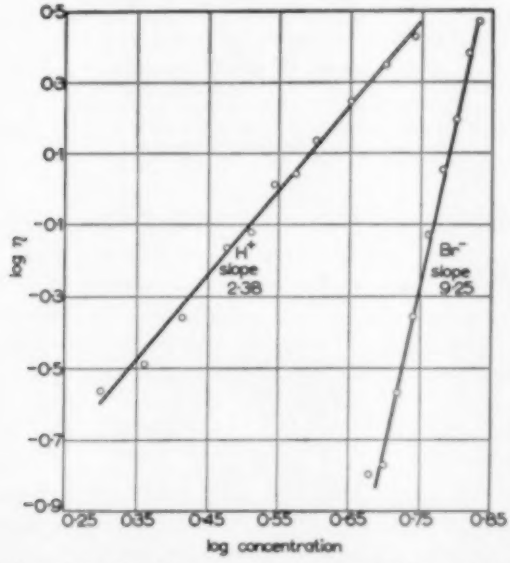

FIG. 9.—Variation of the logarithm of the extraction coefficient with the logarithm of the hydrogen and bromide ion concentrations for protactinium. Hydrogen ion effect at a constant total bromide concentration of 6 M, using hydrobromide acid in sodium bromide mixture. Bromide ion effect at a constant hydrogen ion concentration of 4·5 M.

Fig. 9. The latter effect could not be studied in solutions at constant ionic strength, and activity coefficient data are not available for the sodium bromide–hydrobromic acid mixtures.

IV. *Sulphuric acid solutions*

Only a few cases have been investigated of solvent extraction from sulphuric acid, although several cases have been reported of the enhancement of extraction from other acids by addition of sulphuric acid. The extraction of protactinium from a solution

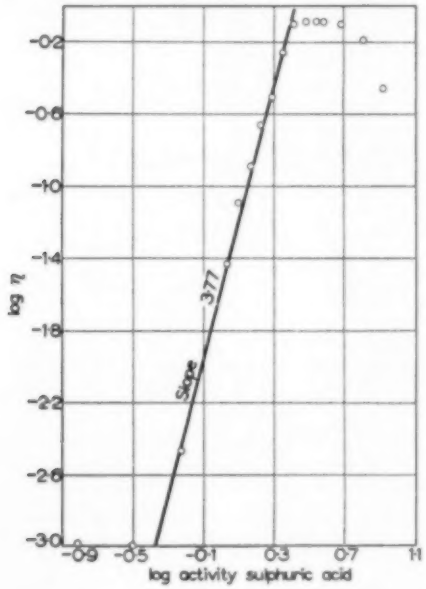

Fig. 10.—Extraction of protactinium-233 into di-*iso*propylcarbinol from sulphuric acid solutions. Variation of the logarithm of the extraction coefficient with the logarithm of the mean ionic activity of the sulphuric acid.

in this acid has already been observed.[2,12] Whereas the graph of percentage extraction against sulphuric acid concentration passes through a maximum and then decreases only slightly if hydrochloric acid is also present in pure sulphuric acid solutions the extraction falls sharply above 6 M acid. Measurements could not be extended beyond 7·5 M because of miscibility of the two phases. A logarithmic plot of the extraction coefficient against the sulphuric acid activity is shown in Fig. 10.

V. *Oxalic acid solutions*

Amongst organic reagents oxalic and citric acids are considered to form the strongest complexes with protactinium, but in contrast to the effect of fluoride ions under certain conditions the addition of oxalic acid has been found to enhance the extraction of protactinium from hydrochloric acid.[12] The effect is most noticeable when the extraction of protactinium in the absence of the oxalic acid is small. A typical curve for a constant hydrochloric acid concentration of 2 M is shown in Fig. 11. It is seen that a very small concentration of oxalic acid markedly increases the extraction. Further increase in the oxalic acid concentration, however, causes the extraction to pass through a maximum and then to fall to a value approximating to that found

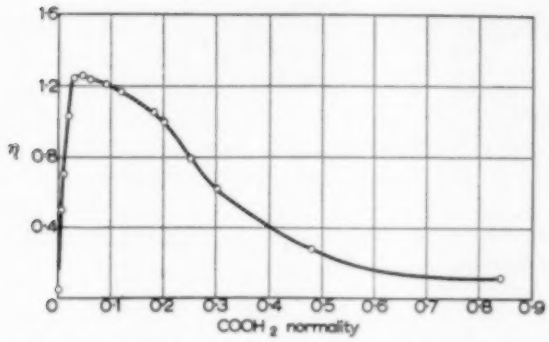

FIG. 11.—Extraction of protactinium-233 into di-*iso*propylcarbinol from 2 N hydrochloric acid + varying amounts of oxalic acid. Variation of the extraction coefficient with the normality of the oxalic acid in the aqueous phase.

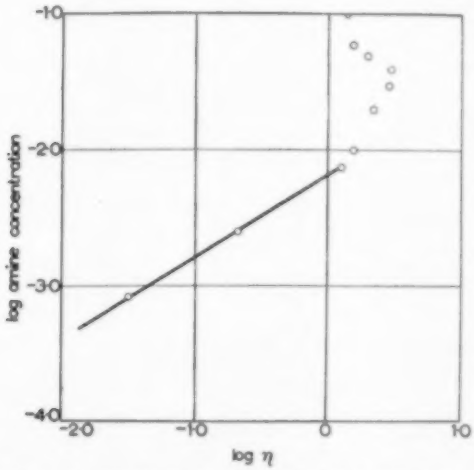

FIG. 12.—Extraction of protactinium-233 from 4·375 N hydrochloric acid into solutions of tribenzylamine in nitrobenzene. Variation of the logarithm of the extraction coefficient with the logarithm of the mole fraction of the amine in nitrobenzene.

for pure hydrochloric acid. The previously-reported[12] suppression of the extraction of protactinium from these solutions by addition of a small but macroscopic amount of niobium has been investigated, but it has not proved possible to repeat this observation. It is suggested that this effect might have been due to niobium initiating the condensation polymerization of the protactinium tracer used. Addition of niobium is almost as effective as increasing the protactinium concentration in accelerating the onset of the hydrolytic-condensation reaction. (See Part IV.)

VI. *Extraction by solutions of tribenzylamine*

Solutions of tribenzylamine have been shown to extract protactinium from hydrochloric acid solutions. The dependence of the extraction coefficient on the concentration of amine in the organic phase may, under certain circumstances, determine the charge on the anionic extracting species. Fig. 12 shows the variation of the extraction

coefficient for protactinium with the concentration of tribenzylamine dissolved in nitrobenzene.

VII. *Strong acid effect*

If the extracting species ionizes as an acid in the organic phase then, as SALDICK[15] and DIAMOND[16] have shown, the addition of small concentrations of anions of very strong acids to the aqueous phase should reduce the extraction coefficient. The data in Table 1 show the effect of the addition of a small concentration of perchloric acid on the extraction of ^{233}Pa by various solvents.

TABLE 1.—EFFECT OF STRONG ACID ON THE EXTRACTION OF PROTACTINIUM INTO VARIOUS SOLVENTS

Solvent	Dielectric constant	Total acidity	Extraction coefficient at $HClO_4$ concentration of					
			0	0·01 N	0·025 N	0·05 N	0·1 N	0·2 N
Benzyl alcohol	5·1	6·2	0·122	0·108	0·094	0·072	0·065	0·063
Methylhexyl ketone	10	4·5	1·71	0·685	0·553	0·341	0·263	0·234
Di-*iso*propyl-carbinol	Approx. 13	3·5	1·63	1·224	1·022	0·775	0·611	0·530
Acetophenone	17·4	4·5	2·57	0·967	0·769	0·621	0·460	0·284
2:2′-dichloro-diethyl ether	21·2	7·2	3·07	0·500	0·295	0·162	0·126	0·105
o-Nitrotoluene	27·4	7·2	2·49	0·362	0·120	0·096	0·054	0·042
Nitrobenzene	34·8	9·0	8·32	2·12	1·102	0·489	0·221	0·125

DISCUSSION

Before dealing with the interpretation of the results one detail of the measurements requires comment. Both the niobium and the tantalum tracer solutions contained oxalate ions and oxalic acid has been shown to enhance the extraction of niobium as well as of protactinium.[12] However, the oxalate concentrations in the solutions actually used in the experiments which contained only a very small proportion of the tracer solutions, were so low that it is considered unlikely that they could have had an appreciable effect on the results. In all cases the final oxalate concentration was much less than 0·001 M.

1. *The chloro-complexes of niobium and protactinium*

It is convenient to consider the results reported in this paper in conjunction with those already given in Parts III and IV in this series.[2,17] The more accurate data contained in this paper clearly show that the logarithmic extraction coefficient-activity plots for these systems are really sigmoid in detail, the curves falling to lower slopes at both high and low acidities.

The curves for the various ketones shown in Fig. 4, Part III, for instance, prove

[15] J. SALDICK, *J. Phys. Chem.* **60**, 500 (1956).
[16] R. M. DIAMOND, *J. Phys. Chem.* **61**, 75 (1957).
[17] A. T. CASEY and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* In press. **10**, 58 (1959).

that the various protactinium species existing in aqueous hydrochloric acid solutions, between 2 and 8 M, are in dynamic equilibrium, although all the solutions are metastable with respect to an irreversible hydrolytic condensation. (see Part IV). The significance of the slopes of the logarithmic plots is dependent on the nature of the protactinium species present in the organic phases. If the organic phase only contains molecular species, including associated ion pairs, the treatment of IRVING and ROSSOTTI is applicable,[18] accepting the limitation that activity coefficients are taken as unity in their analysis. On the other hand, if dissociated species are present in the organic as well as the aqueous phase the analysis of the data becomes more complicated, as DIAMOND has shown, and common ion effects may be important.[16,19]

(a) *Evidence of dissociation in the organic phase.* Two series of observations provide evidence that when ^{233}Pa is used at a concentration of about 10^{-10} M it is present in a number of organic solvents in the form of a complex anion. It has been shown that although changes in the total concentration of the protactinium over a power of ten, about the region of 10^{-10} M, have no effect on the extraction coefficient from a given hydrochloric acid solution, and similar changes in concentration around 10^{-4} M produce no change in the extraction coefficient of ^{231}Pa from the same hydrochloric acid solution, yet the value of the coefficient for ^{233}Pa is higher than that for ^{231}Pa. (Part III.) The ratio of the extraction coefficients for ^{233}Pa and ^{231}Pa, at respective concentrations of 10^{-10} and 10^{-4} M, for a given hydrochloric acid concentration, is a function of the dielectric constant of the solvent, increasing with this quantity. SALDICK and DIAMOND have shown that such behaviour is to be anticipated, supposing that at the lower protactinium concentration the extracting complex, a strong acid, is almost completely dissociated, although most of the cations in the organic phase are supplied by the weaker hydrochloric acid. At the higher concentration the situation is reversed; only a small fraction of the protactinium complex is dissociated, but this determines the cation concentration in the organic phase. It seems preferable to refer to the cation in these systems, rather than the hydrogen ion, since onium ion formation probably occurs in most cases.

Another common cation effect, characteristic of systems in which the extracting acid is extensively dissociated in the organic phase, is the reduction in the apparent extraction coefficient when small concentrations of a strong acid are introduced with the aqueous phase. The effect of perchloric acid on the ^{233}Pa extraction is shown in Table 1. It resembles closely the results obtained by DIAMOND with molybdenum.[16] The magnitude of the reduction in the apparent extraction coefficient increases with the dielectric constant of the solvent.

Both these observations confirm that at the concentrations used in the ^{233}Pa experiments the protactinium is largely present in the organic phase in an anionic form. Certainly it appears to be true for solvents whose dielectric constant exceeds about ten. It can easily be shown that if the protactinium is at trace concentration, largely dissociated in the organic phase, and if the chloride and cation concentrations in this phase are equal and determined entirely by the hydrochloric acid, then the slope of a $\log \eta - \log a_{\pm}$ plot should be one unit less than the sum of the differences of the average number of hydrogen and chlorine atoms in the species in the two phases, taking the organic phase to contain only the associated complex acids. Hydroxyl

[18] H. IRVING, F. J. C. ROSSOTTI and R. J. P. WILLIAMS, *J. Chem. Soc.* 1906 (1955).
[19] R. M. DIAMOND, *J. Chem. Phys.* **61**, 69 (1957).

groups are taken as −1 hydrogen atoms in the usual way. Thus the slope of such a plot should generally be one unit less in the ^{233}Pa range of concentrations than in the ^{231}Pa range, provided η is independent of the protactinium concentration over a reasonable range about each of the two values used in the measurement of η. The data obtained with nitrobenzene gave parallel plots at about 10^{-10} and 10^{-4} M protactinium (Part III, Fig. 8). Presumably this indicates that the protactinium complex is still extensively dissociated at the higher concentration in this solvent of high dielectric constant. Under contrary conditions with solvents of low dielectric constant the protactinium may be largely present as associated species even in the ^{233}Pa range of concentrations.

(b) *Nature of the protactinium species in the aqueous phases.* There are a number of clues to the nature of the protactinium complexes in hydrochloric acid solution. Electrolytic migration experiments suggest that above 6 M the charged protactinium complexes are all anionic. Below 3 M there are considerable amounts of cationic species and between 3 M and 6 M these are gradually converted to anionic species. These experiments cannot provide information about neutral species,[20,21] although the concentration of the simple halide $PaCl_5$ must be negligible since no extraction takes place with pure carbon tetrachloride at any concentration of acid. However, the partially-hydrolysed neutral species, such as $Pa(OH)Cl_4$, etc. would probably be far less readily extracted by a nonpolar solvent and may well be present in appreciable concentrations.

Ion exchange data (Part III, Fig. 7) confirm that appreciable concentrations of anions are present above 6 M in hydrochloric acid. In fact, the surprising feature is rather the high concentration of acid necessary for considerable exchange. The distribution coefficients are low in the acid range 3–6 M; indeed 3 M hydrochloric acid is satisfactory for elution, while electrolytic migration experiments show appreciable concentrations of anions even at 3 M acid and extraction in the range 3–5 M acid is possible with a variety of solvents. However, it is reasonable to suppose that the singly-charged anionic species, such as $Pa(OH)_2Cl_4^-$ will not compete successfully with the chloride ions for sites on the resin, whereas a more highly charged ion, such as $PaCl_7^{2-}$, will do so. The increasing exchange with the resin with increasing hydrochloric acid concentration, in the range 6–8 M, arises from the conversion of the weakly exchanging singly charged anions into more highly charged species. Otherwise if the protactinium were already predominantly in an exchangeable anionic form an increase in hydrochloric acid concentration should reduce the exchange by competition from the chloride ion in the usual way.

A $\log K_d - \log a_\pm$ plot should in fact show a lower slope than the $\log \eta - \log a_\pm$ plot, the difference being equal to the charge carried by the exchanging anion. KRAUS and MOORE considered $Pa(OH)_2Cl_4^-$ to be a probable exchanging species.[22]

Another method of exploring the charge on an anionic complex which can be extracted by solutions of the higher amines consists in determining the variation of the apparent extraction coefficient with the concentration of amine in the organic phase. Provided the derived ammonium salt is not appreciably ionized in the organic

[20] A. G. MADDOCK and G. L. MILES, *J. Chem. Soc.* S 248 (1949).
[21] J. C. SULLIVAN, P. A. SELLERS and E. C. JARDA, quoted by R. E. ELSON in *Radiochemical Studies: The Fission Products* (Edited by J. J. KATZ and G. T. SEABORG). NNES, Plutonium Project Record, Div. IV, Vol. 14A, p. 122. McGraw-Hill, New York (1957).
[22] K. A. KRAUS and G. E. MOORE, *J. Amer. Chem. Soc.* **72**, 4293 (1950).

phase the plot of log η vs. log (concentration of amine) should be linear, with a slope equal to the charge carried by the anionic species extracted, at least at low concentrations of amine. The data obtained with tribenzylamine, Fig. 12, are hardly compatible with this analysis. If, however, ionization of the ammonium salt takes place in the organic phase a much more complicated expression for the slope of the above plot is obtained, because common cation effects in the organic phase eventually lead to a reduction in the extraction coefficient. If it is supposed that the extracting species is present at trace concentrations, that the ammonium species in the aqueous phase are almost completely ionized, and that the chloride and hydrogen ion concentrations in the aqueous phase are maintained equal throughout the measurements, then it can be shown that the slope of the above plot should approach the charge on the anion at very low concentrations of amine. The data of Fig. 12 are more in keeping with this interpretation, but do not provide a conclusive value for the charge on the anion. It might be one or two. It is not surprising that such ionization effects become important with nitrobenzene as diluent. It will be observed that the slope of a log η — log $a_{\pm}$ plot for an extractant consisting of a solution of tributylamine in benzene is 3·7 (see Part III, Fig. 9), not very different from the value, 3·5, for di-*iso*propyl carbinol. (Fig. 1.) There are, however, the strongest reasons for supposing that the anions of the complex acids extracted by any solvents other than those of very high dielectric constant will always carry only a single charge. Even the neutral complex acids must exist as ion pairs in the solvent phase and the electrostatic term in the free energy of transfer from the aqueous to the solvent phase becomes very unfavourable indeed for charges higher than one on the cation and anion. All the data on the extraction of the complex halo acids of the other elements support this contention.[2]

(c) *Spectroscopic data on the chloro complexes.* The close similarity of the niobium and protactinium extraction curves (Figs. 1, 2 and 3) might be taken to indicate that in hydrochloric acid systems giving equal extraction coefficients for the two elements similar proportions of corresponding complexes exist in the pairs of phases. Now KANZELMEYER *et al.*[23] have shown that between 6 and 12 M in hydrochloric acid the dominant niobium species is probably $Nb(OH)_2Cl_4^-$ Salts of this acid are known which have allowed the ultra-violet absorption spectrum of the anion to be identified. The spectrum consists of an intense absorption band with a maximum near 210 mμ, together with a longer wavelength band with its maximum at 281 mμ. In solutions of equal acidity but lower chloride concentration, the cation $Nb(OH)Cl_3^+$ appears and the 281 mμ band is replaced by a band at 260 mμ. At high chloride concentration but lower acidity $Nb(OH)_2Cl_3$ formation takes place, followed by hydrolytic condensation and colloid formation. But between 4 and 6 M in hydrochloric acid a solution was obtained which showed only the lower wavelength absorption; it was suggested that this solution contained principally $Nb(OH)_2Cl_3$. Solutions of protactinium in 6 M or stronger hydrochloric acid, however, show only an intense band with its maximum below 210 mμ (see Part IV, Figs. 1 and 2). A band at 260 mμ only appears once irreversible condensation hydrolysis sets in. However, below 6 M there is evidence of a band, appearing as a shoulder on the lower wavelength band, which appears to have its maximum at about 225 mμ. The formation of the species responsible for this absorption is a reversible process. The spectrophotometric data for the

[23] J. H. KANZELMEYER, J. RYAN and H. FREUND, *J. Amer. Chem. Soc.* **78**, 3020 (1956).

protactinium solutions are thus appreciably different from the corresponding niobium data and suggest that the protactinium species are less hydrolysed.

(d) *The slopes of the extraction coefficient-activity curves.* Theory requires that the sum of the slopes of the logarithmic plots of the apparent extraction coefficient against the concentration of hydrogen and chloride ions is nearly equal to the slope of a similar plot against the hydrochloric acid concentration. Thus in the case of the protactinium data for di-*iso*propyl carbinol the respective slopes are 1·60, 5·20, 6·88. (Calculated from data shown in Figs. 2 and 3.) When activities are used the slopes are naturally much less but additivity cannot be checked, because data are not available for the variation of the chloride activity. The slopes of the $a_{\pm}$ plots for hydrogen ion and hydrochloric acid activities are 1·39 and 3·52 respectively (Fig. 1) for protactinium so that the chloride ion slope is 2·13 by implication. The log η—log $a_{\pm}$ slope for niobium in hydrochloric acid with di-*iso*propyl carbinol is 3·45. Neither the hydrogen nor the chloride activity slopes can be measured in this case, but since the concentration curves are parallel to the protactinium data they are probably much the same as for protactinium.

The ketones generally give a rather steeper log η–log $a_{\pm}$ slope for protactinium (see Part III, Fig. 4) but a solution of tributylamine in benzene gives much the same slope (3·7) as di-*iso*propyl carbinol (see Part III, Fig. 9). Tributyl phosphate gives the rather low slope of 2·4 (Calculated from data given in Part III). A satisfactory interpretation of these data must therefore account for

(α) Different log η–log $a_{\pm}$ slopes in the same acidity range by different types of solvent.

(β) Different log η–log $a_{\pm}$ slopes in different acidity ranges.

(γ) The variation of the extraction coefficient with the hydrochloric acid concentration in a region where the protactinium or niobium are already almost all in the anionic state.

Consider first the case of niobium. Spectroscopic data indicate that niobium is present in the relevant acid range (6–8 M) principally as $Nb(OH)_2Cl_4^-$ and possibly $Nb(OH)_2Cl_3$. It is not certain whether at the concentration of niobium used the organic phase is still largely ionized, but the dielectric constant of di-*iso*propyl carbinol (~13) is not too low, so that in view of the resemblance to the protactinium data ionization will be assumed. Now if the acid extract is $HNbCl_6$ an aqueous phase consisting entirely of $Nb(OH)_2Cl_4^-$ will lead to chloride and hydrogen ion slopes of 2 and 2, $NbOHCl_5^-$ will give 1 and 1, while $Nb(OH)_2Cl_3$ will give 2 and 3. Thus an average composition of equal parts of $Nb(OH)_2Cl_4^-$ and $Nb(OH)_2Cl_3$ approximately would account for the observed slopes and would not be inconsistent with the spectroscopic data. However, it is hardly reasonable to suppose that the average composition of the aqueous phase should remain constant over the range of acidities represented by one of the plots, so that it seems more likely that two species can be extracted, say $HNbCl_6$ and $HNb(OH)Cl_5$, so that the average compositions of both the aqueous and the organic phases change with the acidity, although the difference in average composition remains constant. It remains to justify the postulate that the ion pair $H^+NbCl_6^-$ and possibly $HNb(OH)Cl_5$, are readily extracted into the solvent, while $HNb(OH)_2Cl_4$ is not. This postulate is entirely in keeping with the

model for the extraction process advanced in Part III of this series. The favourable free energy term in the transfer of the ion pair or anion from the aqueous to the organic phase is largely due to the re-formation of the water lattice in the hole that the ion pair or anion vacates. $NbCl_6^-$ probably occupies a larger hole than $Nb(OH)_2Cl_4^-$, but more important, it does not participate in the water structure to the same extent as the latter ion so that a more extensive reorganization of the water structure follows its extraction by the organic solvent.

TABLE 2

Acid range (M)	Protactinium species in decreasing order of concentration from left to right
3	$Pa(OH)Cl_3^+$
3–6	$Pa(OH)Cl_3^+$, $Pa(OH)_2Cl_3$, $Pa(OH)_2Cl_4^-$ changing to $Pa(OH)_2Cl_4^-$, $Pa(OH)_2Cl_3$, $Pa(OH)Cl_2^+$.
6	$Pa(OH)_2Cl_4^-$, $Pa(OH)Cl_5^-$, $PaCl_6^-$.
Very high concentrations	Some $PaCl_7^{2-}$.

With protactinium in solutions above 6 M in hydrochloric acid it seems probable that the aqueous phase contains $Pa(OH)_2Cl_4^-$, $Pa(OH)Cl_5^-$ and possibly some neutral species. The slope for tributylamine in benzene is consistent with the extraction of the ammonium salt of the $PaCl_6^-$ anion from an aqueous solution containing largely the first of these species. The spectroscopic data on the aqueous phase, however, do not indicate such a hydrolysed species. In 3–5 M acid where di-*iso*propyl carbinol is an effective extractant it may still be supposed that the organic phase contains $PaCl_6^-$ and possibly $PaOHCl_5^-$ anions. An aqueous phase composed of an admixture of $Pa(OH)Cl_3^+$, $Pa(OH)Cl_4$ and some $Pa(OH)_2Cl_4^-$ can then account for the observed slopes.

The higher slope of the ketone plots may be partly due to absence of ionization in the organic phase, such solvents having low dielectric constants; this will increase the slope by one unit. However, the ketone slopes are found to be about 5·4, or nearly 2 units higher than di-*iso*propyl carbinol in the same or a higher acidity range. Since the distribution of complexes must be constant at a given concentration of hydrochloric acid, this suggests that the ketones extract more $HPaCl_6$ than $HPa(OH)Cl_5$. The anomalously low slope of tributyl phosphate (2·4, Part III) probably arises from the extraction of a complex of the neutral species $Pa(OH)Cl_4$. These conclusions are summarized in Table 2.

The last of these species may account for the observation that at very high activities, even in solvents of low mutual miscibility, some reduction in the extraction of protactinium occurs (see also the extraction of sulphates and oxalates below).

One important factor has been completely ignored in this analysis of our data. The changing activity of water in the aqueous phase must influence the formation of the extracting species, since this appears to be essentially the reversal of a hydrolytic reaction, and also the formation of the cationic species in the organic phase, since these appear to contain water. These two effects work in opposite directions and although the activity of the water in the aqueous phase can be estimated it is not

possible to decide the overall effect of this factor on the slopes of the logarithmic extraction coefficient plots.

The bromide data cannot be separated into the hydrogen and bromide ion contributions but the overall dependence on a_+ in hydrobromic acid suggests that the aqueous phase contains largely $Pa(OH)Br_5^-$ above 7 M in hydrobromic acid, assuming that $PaBr_6^-$ exists in the organic phase.

2. *The effect of fluoride ions on the extraction*

Clearly the influence of fluoride on the protactinium distribution is quite different from that found for the other two elements. The simplest explanation of the protactinium data is to assume that none of the fluorine containing complexes are extractable. Under these conditions, if complexes containing more than two fluorine atoms are unimportant a plot of $X - 1/(HF)$ against (HF), where X is the ratio of the extraction coefficient with and without fluoride at a concentration (HF), should be linear. In fact, a plot of this function for the data obtained for protactinium is strongly convex towards the (HF) axis. This result indicates that if the assumption that none of the fluoride complexes is extracted is valid, complexes with more than two fluorine atoms become important at quite low fluoride concentrations.

An interesting feature of the enhanced extraction of niobium in the presence of hydrofluoric acid is the low value of the slope $\frac{\delta(\log \eta)}{\delta(\log\ HCl)}$ ~1·5 at constant concentration of hydrofluoric acid, and the slope $\frac{\delta(\log \eta)}{\delta(\log [HF])}$ ~0·5 at constant concentration of hydrochloric acid.

The most plausible hypothesis to account for these observations is the following. $Nb(OH)_2Cl_4^-$ reacts readily with fluoride to produce $NbF(OH)Cl_4^-$ and $NbF_2Cl_4^-$. There is no reason why the latter, which may be formed more readily than $NbCl_6^-$, should not be extracted equally well. There is however no appreciable tendency for niobium to increase its co-ordination number. Thus the addition of hydrofluoric acid enhances the extraction of niobium, the extraction coefficient increasing both with hydrofluoric acid and hydrochloric acid concentration. On the other hand the protactinium complexes react even more readily with fluoride, the hydroxyl groups being replaced by fluorine atoms, but the metal atom readily increases its co-ordination number to seven, or possibly eight, and the unextractable anions of the group $PaCl_xF_{7-x}^{2-}$ become the dominant species in solution.

This suggestion finds support in the observation that, since even doubly charged species can be extracted with very basic solvents of favourable dielectric constant, protactinium can be extracted even from fluoride solution by butanol. The movement of fluoroprotactinate by butanol on paper chromatography has already been reported by LEDERER.[25,26] Tributylamine in benzene, however, is unable to extract the fluorocomplex of protactinium.

3. *Extraction of protactinium from sulphuric and oxalic acids*

The slope of logarithmic extraction coefficient–activity plot for sulphuric acid (Fig. 2) is 3·77. This is quite consistent with the organic phase containing principally

[24] H. A. C. MACKAY, AERE/C/R 884. (1952).
[25] M. LEDERER and J. VERNOIS, *C. R. Acad. Sci. Paris* **244**, 2388 (1957).
[26] G. VERNOIS, *J. Chromatog.* **1**, 52 (1958).

$Pa(SO_4)_3^-$ and the aqueous phase $Pa(SO_4)_2(OH)_2^-$ and possibly $Pa(SO_4)_2OH$. In more strongly acid solution the extraction coefficient begins to drop rapidly; this might reasonably be due to the formation of $Pa(SO_4)_4^{3-}$. Evidence of a sparingly soluble potassium salt of some such sulphatoprotactinate ion has already been reported and an analysis of this compound will shortly appear.[27,28]

The oxalic acid extraction can be interpreted in much the same way. In this case however the extraction only takes place in the presence of hydrochloric acid. $PaCl_4Ox^-$ may well be the extracted species, while both $PaOx_3^-$ and $PaOx_4^{3-}$ may not be extracted, the former because it can be too extensively hydrogen bonded with the water structure and so be prevented from being extracted in the same way as is $Pa(OH)_2Cl_4^-$. Other evidence for such complex oxalates has already been reported by WELCH.[29]

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[27] G. BONISSIERES and M. HAISSINSKY, *Bull. Soc. Chim. Fr.* **18**, 557 (1951).
[28] A. G. MADDOCK and C. MIRANDA. Unpublished work. (1958).
[29] G. A. WELCH, Thesis, London (1956).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 306 to 318. Pergamon Press Ltd. Printed in Northern Ireland

THE EXTRACTION OF SOME METAL CHLORIDES INTO TRI-*n*-BUTYL PHOSPHATE

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Abstract—The extraction of the chlorides of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+} and In^{3+} from hydrochloric acid into a mixture of tri-*n*-butyl phosphate and diluents has been studied using radioactive tracers except for nickel, copper and uranium, which were determined spectrophotometrically. The formula of the species extracted from a solution of cobalt in hydrochloric acid was found to be $CoCl_2 \cdot 2TBP$. The extraction of hydrochloric acid itself has been compared with that of nitric acid under comparable conditions.

IN contrast to the very extensive data concerning the extraction of metals from their solutions in nitric acid and alkali nitrates into tri-*n*-butyl phosphate (TBP), comparatively little has been published concerning extraction systems involving other mineral acids.

PEPPARD *et al.*[1] have investigated the separation of uranium, protactinium and thorium by extraction with TBP from hydrochloric acid solution, but their values of the distribution coefficient for uranium differ somewhat from the unpublished results quoted by HYDE,[2] who reports values of 40 and 2000 for the distribution coefficient (o/a) between TBP and 5 M and 11·8 M hydrochloric acid respectively. GRAY[3] has compared the distribution coefficients for the actinides and lanthanides from 12 M hydrochloric acid into TBP. HEALY and BROWN[4] have examined the extraction of alkali chlorides and LEVITT and FREUND[5] the extraction of zirconium chloride into the same solvent.

In this paper, preliminary data for the extraction of zinc, indium, and uranium, and the transition metals, iron, cobalt, nickel, copper and manganese from their solutions in aqueous hydrochloric acid into TBP are presented together with a more detailed study of the system $CoCl_2$–H_2O–HCl–TBP–Diluent. In addition, the extraction of hydrochloric acid itself into TBP has been considered.

EXPERIMENTAL

Purification of TBP

The TBP was purified by a modification of HEALY and BROWN's method,[4] which was preferable to that of MCKAY[6] in that it gave a perfectly dry solvent rather than one saturated with water. Commercial TBP was stirred with an equal volume of 4 per cent aqueous NaOH for several hours, during which period successive portions of a 4 per cent solution of potassium permanganate in 4% NaOH were added until there was a permanent pink colour in the organic layer. The TBP layer was

[1] D. F. PEPPARD, G. W. MASON and M. V. GERGEL, *J. Inorg. Nucl. Chem.* **3**, 370 (1957).
[2] E. K. HYDE, *Proceedings International Conference Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 281. United Nations (1956).
[3] P. R. GRAY, unpublished results quoted in Ref. 2.
[4] T. V. HEALY and P. E. BROWN, AERE/C/R-1970 (1956).
[5] A. E. LEVITT and H. FREUND, *J. Amer. Chem. Soc.* **78**, 1545 (1956).
[6] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).

separated and washed three times with an equal volume of water. The TBP was finally distilled *in vacuo* over a little solid sodium bicarbonate, the portion coming over between 170° and 180°C at 25 mm Hg pressure being collected.

Dilution of TBP

The work reported here was carried out using TBP diluted with 'odourless' kerosene or with benzene of crystallizable purity.

Partition measurements

(a) *For the* TBP–HCl *system alone.* Twenty millilitres of TBP (or TBP diluted with kerosene) and 20 ml of hydrochloric acid were equilibrated by being stirred together in a centrifuge tube for about 15 min. The phases were then centrifuged and separated for measurements of the partition coefficient.

The water in the organic phase was determined by titration with Karl Fischer's Reagent. Hydrochloric acid was determined by titration with standard alkali solution. The acid content of the organic phase was removed by back extraction into water and determined by titration. Densities were measured by weighing known volumes of the organic phase.

(b) *Partition experiments using radioactive tracers.* Because of the large volume changes which occur on equilibrating TBP with HCl, partitions were carried out using TBP and HCl which had been pre-equilibrated by stirring equal volumes together for about 10 min. Two millilitres of each pre-equilibrated phase were placed in a centrifuge tube and stirred with a small amount of radioactive tracer (total metal concentration in each phase $\sim 10^{-6}$ M) for about 5 min; this time had been shown to be long enough for equilibrium to be reached. After equilibration, the tubes were centrifuged and the phases separated. To determine the concentration of metal in each phase aliquot portions were taken (5–500 μl, depending on the amount of activity present) using calibrated micro-pipettes, and evaporated down on small thin-glass counting trays, taking appropriate precautions to prevent any losses. Analyses for cobalt, iron, manganese, zinc and indium were carried out by counting the β,γ-radiation from ^{60}Co, ^{59}Fe, ^{56}Mn, ^{65}Zn and ^{114m}In using an end-window counter.

(c) *Other partition measurements.* For partitions with nickel, copper and uranium, where the total metal concentration was of the order of 0·02 M, the concentrations of metal in each phase were determined absorptiometrically: nickel by using dimethyl glyoxime, copper using 2:9-dimethyl–1:10-phenanthroline (neocuproine) and uranium using 8-hydroxyquinoline. Analyses for cobalt (other than by radiochemical means) were carried out using Nitroso-R salt.

All partitions were carried out at 21 ± 0·1°C.

RESULTS AND DISCUSSION

(1) *The system* TBP + HCl + H_2O + *diluents*

The results of equilibrating mixtures of aqueous hydrochloric acid and pure TBP, or TBP diluted with 'odourless' kerosene, are given in Table 1. In contrast to the TBP–HNO_3 system reported in some detail by McKay *et al.*,[6] 'odourless' kerosene is of little use as a diluent in the hydrochloric acid system because at acid concentrations greater than 5 M, the TBP–HCl complex that is formed is only moderately soluble in this diluent and three phases result. However, benzene and carbon tetrachloride have been found to be suitable diluents.

It can be seen from Fig. 1 that as the initial concentration of hydrochloric acid increases, the equilibrium concentration of HCl in the organic phase, $[HCl]_o$, is initially small but increases rapidly with the equilibrium concentration of HCl in the aqueous phase, $[HCl]_w$. It can also be seen, by comparison with the results for nitric acid, that although it is initially less than for nitric acid, the extraction of hydrochloric acid into TBP increases rapidly with its concentration in the aqueous phase at and above 5 M.

By applying Walden's equation, $\Lambda\eta/60 = \alpha$, to measurements of the conductivity,

TABLE 1(a).—THE PARTITION OF HYDROCHLORIC ACID BETWEEN AQUEOUS SOLUTIONS AND PURE TBP

$[HCl]_w$	$[HCl]_o$	ΔV	$[H_2O]_o$	q	$\frac{[H_2O]_o}{[HCl]_o}$
0	0	0·5	3·310	—	—
1·02	0·042	0·55	3·370	0·041	—
1·88	0·176	0·75	3·900	0·094	2·63
2·63	0·471	1·05	5·325	0·178	4·64
3·34	0·904	1·30	6·513	0·271	4·23
3·86	1·357	1·70	7·757	0·351	4·07
4·52	1·773	1·90	8·561	0·392	3·79
4·95	2·299	2·10	9·210	0·464	3·44
5·67	2·877	2·40	9·817	0·507	3·05
6·25	3·377	2·60	9·750	0·540	2·81
6·86	3·742	—	—	0·545	—
8·28	4·520	—	—	0·546	—
11·50	4·470	—	—	0·389	—

TABLE 1(b).—THE PARTITION OF HYDROCHLORIC ACID BETWEEN AQUEOUS SOLUTIONS AND SOLUTIONS OF TBP IN KEROSENE

TBP (%)	$[HCl]_w$	$[HCl]_o$	$[H_2O]_o$	TBP (%)	$[HCl]_w$	$[HCl]_o$	$[H_2O]_o$
50	0	0	0·872	20	0	0	0·167
	1·06	0·006	0·892		1·06	0·0004	0·182
	2·03	0·026	0·897		2·06	0·0017	—
	3·00	0·094	1·094		3·10	0·0058	0·186
	4·00	0·244	1·651		4·24	0·020	0·212
	4·80	0·465	2·340		5·15	0·069	0·344
5*	2·06	1×10^{-4}	—				
	3·10	$2·8 \times 10^{-4}$	—				
	4·24	$8·0 \times 10^{-4}$	—				
	5·22	0·0012	—				

* These data were obtained titrimetrically and give the order rather than the absolute values of $[HCl]_o$ which would be better obtained conductimetrically.

TABLE 1(c).—THE PARTITION OF HYDROCHLORIC ACID BETWEEN AQUEOUS SOLUTIONS AND SOLUTIONS OF TBP IN BENZENE

$[HCl]_w$	6·32	8·40	10·12	12·76
$[HCl]_o$	0·003	0·022	0·08	0·158

$[HCl]_w$ is the molar concentration of hydrochloric acid in the aqueous phase and $[HCl]_o$, $[H_2O]_o$ are the molar concentrations of hydrochloric acid and water in the organic phase. ΔV is the change in volume of the organic phase (always positive) after equilibration of 10 ml of each phase. $q = [HCl]_o/[HCl]_w$.

Λ, and viscosity, η, it was shown that the degree of dissociation, α, was always less than 0·1 per cent. This value is of the same order as that found for nitric acid in TBP.[6]

The values for the concentration of water in the organic phase, $[H_2O]_o$, obtained

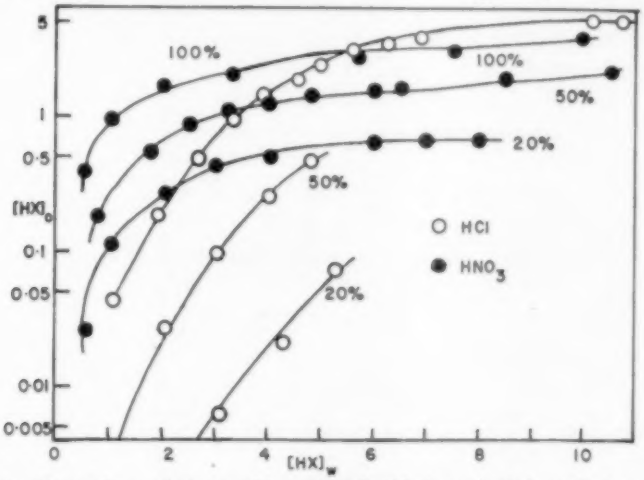

FIG. 1.—Comparison of the partition of hydrochloric and nitric acids into TBP and TBP–kerosene mixtures.

by measurements using Karl Fischer's reagent are compared in Fig. 2 with those obtained by McKAY *et al.* for the TBP–HNO_3 system. From these results it will be seen that a considerable amount of water is extracted with the hydrochloric acid and causes large volume changes.

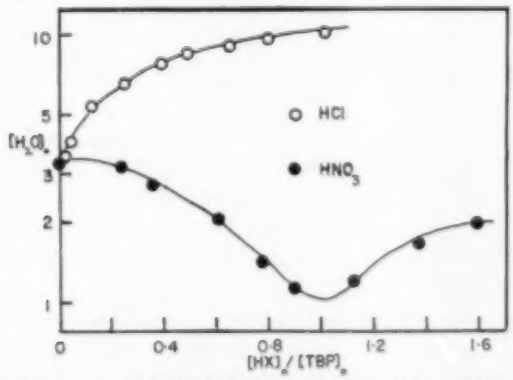

FIG. 2.—The water content of the TBP phase in equilibrium with hydrochloric and nitric acids.

When pure TBP is equilibrated with water the change in volume and the results of the Karl Fischer titrations establish that the mole ratio TBP : H_2O is 1 : 1[6,7] suggesting the formation of an ion-association complex which can be formulated TBP → H_2O. McKAY's data from Karl Fischer titrations showed that as nitric acid is extracted into TBP, water is displaced until the amount of nitric acid in the organic phase is sufficient to form TBP → HNO_3. Beyond that acidity other factors apply,

[7] D. J. TUCK, *J. Chem. Soc.* 2783 (1958).

and these have been further discussed by TUCK.[7] Indeed MCKAY found that the ratio $([HNO_3]_o + [H_2O]_o)/[TBP]_o$ was always greater than one, showing that the replacement mechanism is not a simple one.

In the HCl system the simplified picture of an acid displacing water, molecule for molecule, does not apply at all. As the acid is extracted (Fig. 2) there is an appreciable increase in the amount of water in the organic phase above that required to form the monohydrate, $TBP \rightarrow H_2O$. The last column in Table 1 shows the ratio $[H_2O]_o/[HCl]_o$

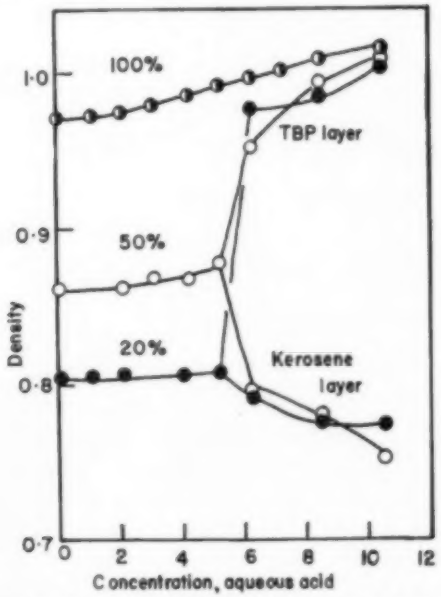

FIG. 3.—The densities of the TBP and TBP–kerosene phases in equilibrium with aqueous hydrochloric acid.

in the organic phase. At low acid concentrations this is of the order of 4 : 1, though at higher acidities this ratio tends to decrease, no doubt due to dehydration and activity effects. Furthermore, at the highest acid concentrations, complexes with more than one molecule of hydrochloric acid per mole of TBP are certainly formed and the entry of these extra HCl molecules into the organic phase will be in competition with the molecules of water already present.

The behaviour of the TBP–HCl system is very similar to that of the ethers–halogen acids systems investigated in this laboratory by IRVING and ROSSOTTI.[8] The systems have a common feature in that they all involve oxygen-donor solvents and exhibit large volume changes. Because of these large volume changes it would be unjustifiable to attempt any detailed analysis of the equilibria without first carrying out a great deal of work on the activities of hydrochloric acid and water in TBP.

Effect of diluents. In order to reduce the values of effective distribution coefficients, 'odourless' kerosene is commonly used as an inert diluent for extractions with TBP from nitric acid of any concentration. Carbon tetrachloride, benzene, hexane and other hydrocarbons are equally serviceable and it would appear that $TBP \rightarrow HNO_3$

[8] H. IRVING and F. J. C. ROSSOTTI, *J. Chem. Soc.* 1946 (1955).

is completely miscible with these solvents. This is not the case with the complex TBP → HCl, for the use of kerosene is restricted in the system TBP–H_2O–HCl to acidities below 5 M HCl. Above this concentration three phases separate, the uppermost of kerosene containing very little water or acid, and a middle layer of TBP saturated with water and acid but containing little kerosene. This is shown as a function of the densities of the organic phases in Fig. 3. On the other hand simple two-phase systems were obtained over the whole accessible range of HCl concentrations when benzene or carbon tetrachloride were used as inert diluents. Data for the

TABLE 2.—THE DISTRIBUTION COEFFICIENTS OF SOME TRANSITION AND OTHER METALS BETWEEN AQUEOUS HYDROCHLORIC ACID AND TBP

Acid strength M	Ni^{II}	Mn^{II}	Cu^{II}	Co^{II}	Zn^{II}	UO_2^{II}	In^{III}	Fe^{III}
1·06			0·0039			0·353	4·57	
2·06				0·0014	34·11			378
3·10	0·0030	0·014	0·156	0·0055	34·22	4·83	96·1	
4·24				0·0265				
5·22	0·0043	0·026	0·363	0·103	21·70	33·59	165	
6·29				0·320			200	
7·25	0·0053	0·060	0·493	0·640	7·82	70·17	171	
8·55	0·0044		0·498	1·030				437
9·60	0·0038	0·115	0·500	1·15	3·31	60·80	61·0	
10·60		0·124	0·449	1·23		48·80	51·0	763
11·30				0·98				
12·00		0·141						

extraction of HCl into 4% TBP in benzene [Table 1 (c)] over the range 6·34–12·8 M HCl form a smooth continuation of those for 5% TBP in kerosene for the range 2–5 M HCl [Table 1 (b)].

(2) *Solvent extraction of metal chlorides*

Wherever possible, values of the distribution (extraction) coefficient, q, which is defined by

$$q = \Sigma[\text{metal species}]_{\text{organic layer}}/\Sigma[\text{metal species}]_{\text{aqueous layer}},$$

were determined using radioactive tracers. The isotopes used were not carrier free, but the total concentration of metal originally in the aqueous phase was 10^{-6} M. The only analyses which were not determined radiochemically were those for nickel, copper, and uranium; the original concentration of these metals in the aqueous phase was 0·02 M. Results for cobalt were obtained both radiochemically and absorptiometrically and they show the expected differences in the values of q at tracer and macro concentrations, Fig. 5. The values found for the distribution coefficients of some transition and other metals between aqueous hydrochloric acid and TBP are given in Table 2 and shown in Fig. 4.

Consider the divalent metals first. It is obvious that there are considerable variations in their ease of extraction. Whereas the values of q for cobalt and copper

are similar, those for nickel and manganese at the same acidity are very much lower whilst those for zinc are very much higher. This poses some interesting problems of interpretation.

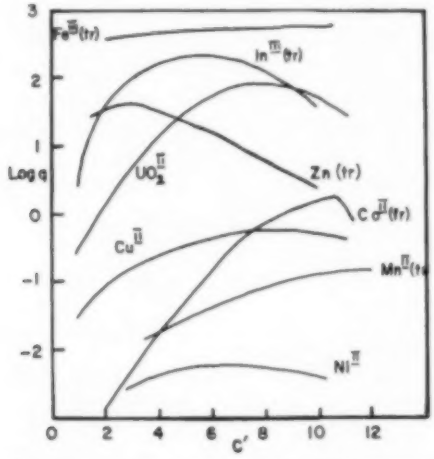

FIG. 4.—The distribution of certain transition metal halides between aqueous hydrochloric acid (concentration c') and TBP.

Little is known about the extraction of divalent metals as nitrates into TBP, but the marked decrease in distribution coefficients on passing from tetravalent to trivalent metals would be expected to continue with divalent and monovalent metals. In the extraction of an n-valent cation, the material extracted is believed to be the

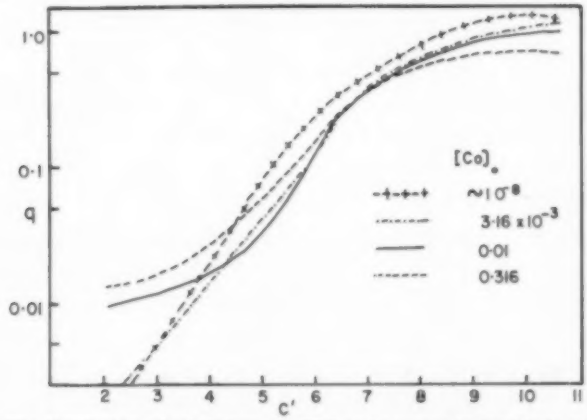

FIG. 5.—The distribution of cobalt between TBP and aqueous hydrochloric acid (concentration c') for various concentrations of metal in the organic phase, $[Co]_o$.

formally neutral species $M(NO_3)_n(6-n)TBP$, where $M = Th^{IV}$, Zr^{IV}, Y^{III}, Pu^{III} etc., and $MO_2(NO_3)_n(4-n)TBP$, where $M = UO_2^{II}$, NpO_2^{II}, NpO_2^{I} etc. With the alkali and alkaline earth metals the degree of solvation by TBP does not follow any regular pattern. On the other hand, in the extraction of metal halides into oxygen-donor solvents acido-complexes are certainly the main extractable species. Thus IRVING and ROSSOTTI,[8] have demonstrated that $HInX_4$, aq is extracted from an

aqueous solution of In^{3+} ions in halogen acids (HX) by a variety of ethers and ketones. Since the tendency to form anionic complexes with the NO_3^- ion is less than with halogen ions, X^-, at least for the cations of lower valency, it would not be surprising that halides of divalent transition metals should extract more readily than their nitrates into oxygen-donor solvents in which category TBP must surely be included. Certainly q for cobalt chloride is at least 1000 times greater than that for cobalt nitrate ($q_{max} = 10^{-3}$)[9] under conditions of maximum extraction.

Cobalt chloride is extracted readily into TBP and q reaches a maximum value of 1·23 in 10 M HCl. The curve of log q against concentration of hydrochloric acid is very similar in shape to the plot of log K_D against concentration of acid for absorption on an anion-exchange resin; moreover the maximum occurs at the same concentration of acid in both cases. KRAUS[10] postulates the adsorption of the ions $CoCl_3^-$ and $CoCl_4^{2-}$ on the resin. The analogue of the resin phase in solvent extraction will be the organic layer. However conductivity measurements show that the extracted species is essentially unionized, so that it becomes necessary to postulate the extraction of solvated acido-complexes of the type $HCoCl_3$, H_2CoCl_4 or a neutral species such as Co_nCl_{2n} (Solvent)$_x$. Nickel, which shows little tendency to form chloro-complexes, is extracted poorly ($q_{max} = 5{\cdot}3 \times 10^{-3}$) compared with cobalt ($q_{max} = 1{\cdot}23$) and zinc ($q_{max} = 33$), which are known to form chloro-complexes with great readiness. Manganese ($q_{max} = 0{\cdot}124$) and copper ($q_{max} = 0{\cdot}5$) show a similar behaviour. Moreover the slope and relative positions of the curves for the distribution of all these metals between hydrochloric acid and an anion-exchange resin closely resemble the pattern for solvent extraction shown in Fig. 4. The position of ferric chloride is anomalous and the behaviour of the system needs further study.

From the point of view of analytical separations the new data suggest a number of useful possibilities. Iron, cobalt and nickel can be easily separated by solvent extraction using TBP. Working in 10 M HCl, $q_{Fe^{III}}$ is 500 times greater than q_{Co}, which is, in turn, 400 times greater than q_{Ni}. Indium and uranium can be separated easily at low acid concentrations, and zinc and uranium at both low and high acid concentrations. Indeed, with the exception of cobalt and copper, all the divalent metals studied can be separated easily from one-another.

(3) *Detailed study of the solvent extraction of cobalt*

The partition of a solute at tracer concentrations does not always follow the same pattern at higher concentrations which will normally be more significant in practical separations. The extraction of cobalt into TBP has therefore been studied over a wide range of metal concentrations. From the results (Fig. 5) it can be seen that from hydrochloric acid solutions of 6 M and above, the value of q tends to increase as the concentration of cobalt decreases. However the change in the value of q as the concentration of metal is increased from 10^{-6} to 10^{-1} M is relatively small and the behaviour at macro concentrations is not significantly different from that at tracer level. From Karl Fischer titrations of the organic phase rich in cobalt it was shown that, in general, as the metal concentration increased the concentration of water decreased.

[9] T. B. PIERCE, Unpublished work.
[10] G. E. MOORE and K. A. KRAUS, *J. Amer. Chem. Soc.* **74**, 843 (1952).

The distribution coefficient of any ion-association complex can be represented by a general equation:[11]

$$q = \frac{\Sigma p_{hmnws}\beta_{hmnws} m[\mathrm{H}]^h[\mathrm{M}]^m[\mathrm{L}]^n[\mathrm{H_2O}]^w[\mathrm{S}]^s}{\Sigma \beta_{h'm'n'w's'} m'[\mathrm{H}]^{h'}[\mathrm{M}]^{m'}[\mathrm{L}]^{n'}[\mathrm{H_2O}]^{w'}[\mathrm{S}]^{s'}} \quad (1)$$

where p_{hmnws} represents the partition coefficient of $\mathrm{H}_{h'}\mathrm{M}_{m'}\mathrm{L}_{n'}(\mathrm{H_2O})_{w'}\mathrm{S}_{s'}$ between the aqueous phase and the organic phase (containing solute S with or without an inert diluent), and h', m', n', w', s' refer to the aqueous phase and h, m, n, w, s refer to the organic phase. Also $\beta_{h'm'n'w's'} = [H_{h'}\mathrm{M}_{m'}\mathrm{L}_{n'}(\mathrm{H_2O})_{w'}\mathrm{S}_{s'}]/[\mathrm{H}]^{h'}[\mathrm{M}]^{m'}[\mathrm{L}]^{n'}[\mathrm{H_2O}]^{w'}[\mathrm{S}]^{s'}$.

If the concentration of metal is sufficiently low it is possible to vary [S] under conditions where [H], [L], and $[\mathrm{H_2O}]$ are effectively constant by varying the concentration of S (in this case TBP) in an inert organic diluent.

Taking logarithms of equation (1) and differentiating partially with respect to the concentration of solvent:

$$\left(\frac{\partial \log q}{\partial \log [\mathrm{S}]}\right)_{[\mathrm{H}][\mathrm{M}][\mathrm{L}][\mathrm{H_2O}]} = \frac{\Sigma p_{hmnws}\beta_{hmnws} s[\mathrm{H}]^h[\mathrm{M}]^m[\mathrm{L}]^n[\mathrm{H_2O}]^w[\mathrm{S}]^s}{\Sigma p_{hmnws}\beta_{hmnws}[\mathrm{H}]^h[\mathrm{M}]^m[\mathrm{L}]^n[\mathrm{H_2O}]^w[\mathrm{S}]^s} - \frac{\Sigma \beta_{h'm'n'w's'} s'[\mathrm{H}]^{h'}[\mathrm{M}]^{m'}[\mathrm{L}]^{n'}[\mathrm{H_2O}]^{w'}[\mathrm{S}]^{s'}}{\Sigma \beta_{h'm'n'w's'}[\mathrm{H}]^{h'}[\mathrm{M}]^{m'}[\mathrm{L}]^{n'}[\mathrm{H_2O}]^{w'}[\mathrm{S}]^{s'}} \quad (2)$$

where the first term on the RHS defines $\bar{\mathrm{S}}_{org}$, tne average number of molecules of the solvent, S, associated with each molecule of the species extracted into the organic phase. The second term on the RHS defines $\bar{\mathrm{S}}_{aq}$, the average degree of solvation (by S) of molecules in the aqueous phase. Hence

$$\left(\frac{\partial \log q}{\partial \log [\mathrm{S}]}\right) = \bar{\mathrm{S}}_{org} - \bar{\mathrm{S}}_{aq} \quad (3)$$

or

$$\log q = (\bar{\mathrm{S}}_{org} - \bar{\mathrm{S}}_{aq}) \log [\mathrm{S}] + \text{constant} \quad (4)$$

If the solute, S, does not associate with metallic species in the aqueous phase, $\bar{\mathrm{S}}_{aq} = 0$ and equation (4) becomes identical in form with that deduced by MCKAY[12] in a less rigorous manner.

Data for the extraction of tracer quantities of ^{60}Co from 6·3 M and from 10·6 M HCl into various mixtures of TBP and benzene are presented in Fig. 6. The experiments were carried out at two concentrations of acid because MCKAY *et al.*[13,14] have noted changes in the number of TBP molecules associated with $\mathrm{Zr(NO_3)_4}$ and $\mathrm{Th(NO_3)_4}$ with change in the acidity of the aqueous phase. In the present case the graphs both have a slope of 2·0, pointing to the presence of two molecules of TBP per molecule of extracted cobalt complex and strongly suggesting that only a single species is extracted.

At first sight this result appears surprising, for the compositions $[\mathrm{M(NO_3)_3}, 3\mathrm{TBP}]$, $[\mathrm{M(NO_3)_4}, 2\mathrm{TBP}]$, and $[\mathrm{MO_2(NO_3)_2}, 2\mathrm{TBP}]$ reported for many trivalent, tetravalent, and '-yl' ions seem to indicate a tendendy to achieve a co-ordination number of six.

[11] H. IRVING, F. J. C. ROSSOTTI and R. J. P. WILLIAMS, *J. Chem. Soc.* 1906 (1955).
[12] H. A. C. MCKAY, *Proceedings International Conference Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 314. United Nations (1956).
[13] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[14] E. HESFORD, H. A. C. MCKAY, D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).

If conditions can be arranged such that [H], [M], [H_2O], and [S] remain effectively constant while [L] is varied it can readily be shown that

$$\left(\frac{\partial \log q}{\partial \log [L]}\right) = \bar{n}_{org} - \bar{n}_{aq}$$

where $\bar{n}_{org}$, $\bar{n}_{aq}$ are the average number of atoms of the ligand, L, per molecule in the organic and aqueous phases respectively.

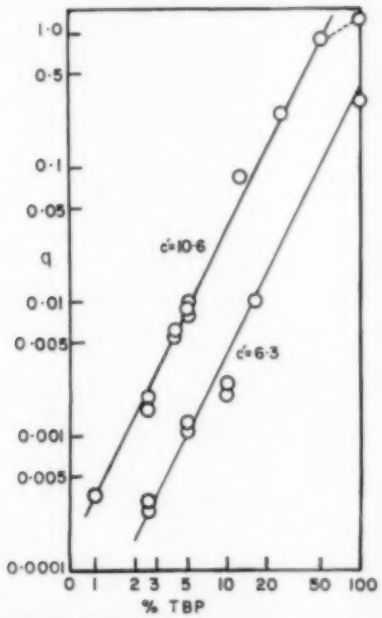

FIG. 6.—The variation in the distribution coefficient, q, for the extraction of cobalt chloride from 6·3 M and 10·6 M hydrochloric acid as a function of the concentration of TBP in the organic phase.

In extractions of cobalt from hydrochloric acid of low molarity we may infer from a knowledge of the relevant stability constants[15] defined by $\beta_n = [CoCl_n]/[Co][Cl]^n$ that $\bar{n}_{aq}$ is not much larger than zero. The plot of log q against the logarithm of the activity of the hydrochloric acid for extraction of tracer ^{60}Co into TBP shown in Fig. 7 has a slope of approximately 2 over a wide range of halide ion concentrations, suggesting a molar ratio metal : chloride of 1 : 2 in the extracted species. Since the concentration of metal was so low in this and in the foregoing experiment it appears reasonable to discount the possibility of polynuclear species. It would appear, therefore, that the extracted species has the composition $CoCl_2$, 2TBP. Alternative formulations such as $[Co(TBP)_4(H_2O)_2][CoCl_4]$ are less probable in view of the very low conductivity of the organic extract and are inconsistent with measurements of absorption spectra described below.

KATZIN and GEBERT[16] have shown that the blue colour of solutions of cobalt

[15] *Stability Constants. Part II. Inorganic Ligands.* The Chemical Society, London (1958).
[16] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **72**, 5464 (1950).

chloride in acetone is due to the tetrahedral complex $[CoCl_2(acetone)_2]$ which is characterised by absorption maxima at 574 and 620 mμ. The pink colour of aqueous solutions of cobalt salts is due to the hexa-co-ordinated ion $Co(H_2O)_6^{2+}$.

We find that a solution of cobalt perchlorate in TBP is pink: but on the addition of lithium chloride a blue colour develops and well marked peaks appear at 580 and 670 mμ with shoulders at 620 and 640 mμ. With increasing amounts of lithium chloride the molar extinction coefficients at 580 and 670 mμ increased but the ratio

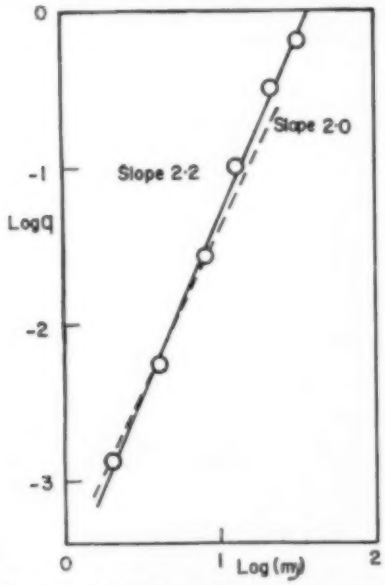

FIG. 7.—The variation in the distribution coefficient of the solvated cobalt complex with the activity of hydrochloric acid.

of the peak heights, $\varepsilon_{670} : \varepsilon_{580} = 2{\cdot}00 \pm 0{\cdot}11$, remained effectively unchanged. The application of Job's method of continuous variations to the system at both 580 and 670 mμ gave maxima between 30 and 33% cobalt, again pointing to a complex containing cobalt and chlorine in the ratio 1 : 2. The composition of the blue species thus appears to be $[CoCl_2(TBP)_2]$ completely analogous to the blue complex identified by KATZIN and GEBERT in acetone solution. Our results are given in Table 3. The same blue complex was identified spectrophotometrically in the organic phase obtained by extracting a solution of cobalt chloride with TBP.

It is perhaps significant that the amount of water in the organic phase decreases markedly as the amount of cobalt extracted increases. This is entirely consistent with the displacement of water from the complex TBP $\rightarrow H_2O$, as it co-ordinates to $CoCl_2$. The blue species is most likely to be a tetrahedral complex $[CoCl_2(TBP)_2]$: its formulation as an octahedral complex containing water, $[CoCl_2(TBP)_2(H_2O)_2]$ is not however excluded by the experimental results, but seems unlikely in view of the spectrophotometric observations.

(4) *Extraction in the presence of lithium chloride*

Cobalt chloride is very much more extractable from slightly acidified solutions of lithium chloride, than from hydrochloric acid of a similar concentration. Lithium

chloride is extracted into TBP to a rather less extent than is hydrochloric acid. For a 5 M solution $q_{HCl} = 0{\cdot}46$ and $q_{LiCl} = 0{\cdot}0052$. The results, given in Table 4, are shown in Fig. 8, where they are compared with the results using hydrochloric acid alone.

These results can be explained in that the hydrochloric acid, the lithium chloride,

TABLE 3.—JOB'S METHOD OF CONTINUOUS VARIATIONS. RESULTS FOR THE SYSTEM $Co(ClO_4)_2$–LiCl–TBP

Cobalt (%)	ε_{555}	ε_{670}
5	0·055	0·329
10	0·098	0·570
15	0·164	0·845
20	0·228	1·120
25	0·400	1·250
27·5	0·525	1·322
30	0·640	1·363
32·5	0·765	1·425
35	0·760	1·355
37·5	0·731	1·280
40	0·675	1·270
50	0·575	1·080
60	0·445	0·835
70	0·317	0·565
80	0·207	0·373

TABLE 4.—THE SALTING OUT EFFECT OF LITHIUM CHLORIDE

Total $[H^+]$	Total $[Cl^-]$			
	5·22	6·29	8·55	10·00
	Distribution coefficient, q			
t*	0·11	0·392	24·04	2407
1·06	0·103	0·339	8·75	
2·06	0·0736	0·245	3·27	99
3·10	0·0595			
4·24		0·168	1·39	15·8
6·29			1·04	6·14
8·55			1·03	

* t signifies trace.

and the cobalt chloride are in competition for the available TBP molecules, as TBP forms solvates with all three electrolytes. As the hydrochloric acid has a larger value of q than lithium chloride it is assumed that it is more strongly bound to the TBP and therefore forms a stronger complex.[17] Hence as hydrochloric acid will compete with cobalt chloride for the TBP molecules more strongly than lithium

[17] E. GLUECKAUF, *Ind. Chim. Belge* **23**, 227 (1958).

chloride, as hydrochloric acid is replaced by lithium chloride the number of free TBP molecules available for complexing with cobalt chloride will increase, and hence the value of q_{Co} will increase. The value of q_{Co} will be greatest when hydrochloric acid has been totally replaced by lithium chloride. This is the case in practice as will be seen from Fig. 8: on replacing 10 M HCl with 10 M LiCl there is nearly a 2000-fold increase in q_{Co}.

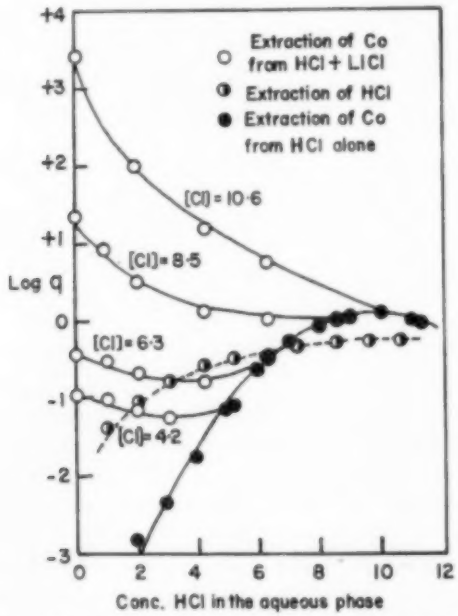

FIG. 8.—The salting-out effect of lithium chloride on the distribution of cobalt chloride between aqueous hydrochloric acid and TBP.

After this work had been completed we became aware of a communication by GAL and RUVARAC to the Institute of Nuclear Science of Belgrade. These authors studied the extraction of a number of metallic chlorides into a solution of TBP in dibutyl ether. Their results for Fe^{3+}, UO_2^{2+}, Co^{2+}, H^+, and Ni^{2+} confirm ours and they also demonstrate that cobalt is extracted with two molecules of TBP. Their results differ only in showing, at macro concentrations, that iron as Fe^{2+} is less extractable than Fe^{3+}.[18]

Acknowledgements—We are grateful to the Royal Society and to Imperial Chemical Industries Ltd. for the loan of apparatus. One of us (D. N. E.) is indebted to the U.K. Atomic Energy Authority for financial assistance.

[18] I. J. GAL and A. RUVARAC, *Bull. Inst. Nucl. Sci. Belgrade* **8**, 67 (1958).

J. Inorg. Nucl. Chem., 1959, Vol. 10, pp. 319 to 322. Pergamon Press Ltd. Printed in Northern Ireland

THE NATURE OF THE NITRATE IN THE TBP SOLVATES $M(NO_3)_3 \cdot 3TBP$, $M(NO_3)_4 \cdot 2TBP$ AND $MO_2(NO_3)_2 \cdot 2TBP$*

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Abstract—An examination of the infra-red spectra of the TBP solvates $M(NO_3)_3 \cdot 3TBP$, $M(NO_3)_4 \cdot 2TBP$ and $MO_2(NO_3)_2 \cdot 2TBP$ has been made, and compared with the infra-red spectra of the corresponding hydrates. It is observed that a considerable decrease in symmetry of the nitrate group has occurred in going from the hydrates to the TBP solvates.

THE extraction of nitrates by tri-*n*-butyl phosphate (TBP) has been extensively studied.[1–10] It has been established that in the extraction of trivalent lanthanide cations a trisolvate is formed, $M(NO_3)_3 \cdot 3TBP$; for tetravalent actinide cations, e.g. Th(IV), Np(IV), Pu(IV), a disolvate is formed, $M(NO_3)_4 \cdot 2TBP$; for hexavalent actinide cations, UO_2(II), NpO_2(II), PuO_2(II), a similar disolvate is formed, $MO_2(NO_3)_2 \cdot 2TBP$.[7] These extractions can proceed either by a mechanism involving ion-pairs or by one involving neutral molecules. HEALY and MCKAY[7] have presented conductivity data for $UO_2(NO_3)_2 \cdot 2TBP$ and the ultra-violet spectra for $UO_2(NO_3)_2 \cdot 2TBP$ and $PuO_2(NO_3)_2 \cdot 2TBP$, which lend support to the conclusion that the extracted species is an unionized neutral molecule, at least in these extractions. Additional information concerning the nature of the nitrate in these compounds can be acquired from an examination of the infra-red spectra of these nitrate complexes. This paper presents the infra-red spectra of the TBP solvates of $La(NO_3)_3$, $Sm(NO_3)_3$, $Sc(NO_3)_3$, $Y(NO_3)_3$, $Ce(NO_3)_3$, $Th(NO_3)_4$, $Ce(NO_3)_4$, and $UO_2(NO_3)_2$. For comparative purposes the spectra of the corresponding hydrates of the above nitrates were also examined.

EXPERIMENTAL

Determination of spectra

The spectra were determined with a Model 21 Perkin–Elmer spectrophotometer. Liquid film spectra of the TBP solvates were determined. The spectra of the nitrate hydrates were made by

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) D. F. PEPPARD, J. FARIS, P. GRAY and G. MASON, *J. Phys. Chem.* **57**, 294 (1953).
(2) D. F. PEPPARD, P. GRAY and M. MARKUS, *J. Amer. Chem. Soc.* **75**, 6063 (1953).
(3) D. F. PEPPARD, G. MASON and J. MAIER, *J. Inorg. Nucl. Chem.* **3**, 215 (1956).
(4) D. F. PEPPARD, W. DRISCOLL, R. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).
(5) J. WARF, *J. Amer. Chem. Soc.* **71**, 3257 (1949).
(6) K. ALCOCK, S. GRIMLEY, T. HEALY, J. KENNEDY and H. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
(7) T. HEALY and H. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).
(8) T. HEALY and H. MCKAY, *Rec. Trav. Chim.* **75**, 730 (1956).
(9) E. HESFORD and H. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).
(10) L. KATZIN, J. FERRARO, W. WENDLANDT and R. MCBETH, *J. Amer. Chem. Soc.* **78**, 5139 (1956).
(11) K. ALCOCK, F. BEDFORD, W. HARDWICK and H. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
(12) D. SCARGILL, K. ALCOCK, J. FLETCHER, E. HESFORD and H. MCKAY, *J. Inorg. Nucl. Chem.* **4**. 304 (1957).
(13) G. BEST, H. MCKAY and P. WOODGATE, *J. Inorg. Nucl. Chem.* **4**, 315 (1957).
(14) E. HESFORD, H. MCKAY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
(15) K. ALCOCK, G. BEST, E. HESFORD and H. MCKAY, *J. Inorg. Nucl. Chem.* **6**, 328 (1958).
(16) T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).

means of KBr disks, Nujol mulls or hexachlorobutadiene mulls. Hexachlorobutadiene (Hooker Electrochemical Co.) was used to check the region between 1250 to 1550 cm^{-1}, and Nujol for lower frequencies.

Materials

(a) $Y(NO_3)_3 \cdot 3H_2O$ was prepared from the oxide obtained from A. D. Mackay & Co.; (b) $Sc(NO_3)_3 \cdot 4H_2O$ was prepared from the oxide obtained from the Argonne National Laboratory (Special Materials Division); (c) $La(NO_3)_3 \cdot 5H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ were obtained from Lindsay Chemical Company; (d) $Ce(NO_3)_3 \cdot 6H_2O$ (Reagent Grade) and $(NH_4)_2Ce(NO_3)_6$ (Reagent Grade) were obtained from the G. Frederick Smith Chemical Company; (e) $Th(NO_3)_4 \cdot 5H_2O$ was recrystallized from H_2O–HNO_3 solution. The crude material was obtained from Lindsay Chemical Company; (f) the $UO_2(NO_3)_2 \cdot 3H_2O$ was obtained from the Special Materials Division of the Argonne National Laboratory; (g) tri-*n*-butyl phosphate was prepared as previously reported.[9]

Preparation of the TBP *solvates*

Saturated solutions of the various nitrates in tri-*n*-butyl phosphate were prepared. The TBP was shaken for 24 hr with excess solid nitrate hydrate, centrifuged and the organic phase separated. The organic phase was again contacted with excess solid, centrifuged and the phases separated. Spectra were then determined on these saturated solutions.

DISCUSSION AND RESULTS

GATEHOUSE[17] and QUAGLIANO[18] have recently examined the infra-red spectra of several nitrato-complexes of the transition elements. They have been able to distinguish between co-ordinated nitrato-groups and the nitrate ion present in these metal complexes. In going from a nitrate ion (point group D_{3h} symmetry) to a covalent nitrate (point group C_{2v} symmetry) a lowering of symmetry occurs.[19] The ν_3 frequency (NO_2 asymmetric stretching) in the symmetrical NO_3^- ion undergoes a splitting into frequencies ν_4 (NO_2 asymmetric stretching, 1481–1531 cm^{-1}), and ν_1 (NO_2 symmetric stretching, 1253–1290 cm^{-1}). In addition, ν_2 at 970–1034 cm^{-1} and corresponding to the N—O stretching (usually inactive in the infra-red for the NO_3^-), appears. The ν_6 frequency at ~800 cm^{-1} is the non-planar rocking frequency. The ionic nitrates of the alkali metals[20] illustrate the point group D_{3h} type of symmetry, where the strong ν_3 frequency is centred in the region of 1380 cm^{-1} and no splitting is observed (Table 1). Methyl nitrate, in which the bonding to the oxygen must be predominantly covalent, shows the point group C_{2v} symmetry. Here the maximum splitting occurs, and ν_4 is at 1672 cm^{-1} and ν_1 is at 1287 cm^{-1}.

It is observed from Table 1 that for all of the TBP solvates investigated, splitting of the ν_3 frequency occurs. The frequency of the absorption band (ν_4) was found to occur between 1487 and 1538 cm^{-1}. The frequency of the absorption band (ν_1) was observed in the region of 1270–1296 cm^{-1}. Both the ν_4 and ν_1 absorption bands in these solvates are strong, and in addition occur as multiple bands in many cases. The absorption band (ν_2) is masked in these TBP solvates because of the presence of overlapping frequencies in the 1000–1100 cm^{-1} region (P–O st., C–O st.). The absorption band (ν_6) is usually weak and is centred at 806–818 cm^{-1}.

[17] B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM, *J. Chem. Soc.* 4222 (1957); C. C. ADDISON and B. M. GATEHOUSE, *Chem. & Ind.* 464 (1958).
[18] J. V. QUAGLIANO, Private communication and paper presented at 132nd Meeting Amer. Chem. Soc., Miami, Florida, April 7–12 (1957).
[19] G. HERZBERG, *Infra-red and Raman Spectra of Polyatomic Molecules* p. 178. Van Nostrand, New York (1945).
[20] F. A. MILLER and C. H. WILKINS, *Analyt. Chem.* **24**, 1253 (1952).

TABLE 1.—INFRA-RED ABSORPTION FREQUENCIES OF SEVERAL NITRATE TBP SOLVATES (LIQUID FILM SPECTRA) AND SEVERAL NITRATE HYDRATES (KBr DISK SPECTRA = *d*, HEXACHLOROBUTADIENE AND NUJOL MULLS = *m*).

Frequencies (cm^{-1})

Point group C_{2v}

TBP solvate	ν_4		ν_1	ν_2	ν_6
$La(NO_3)_3$	1487 (*s*)		1294 (*s*)	?	812 (*w*)
$Ce(NO_3)_3$	1501 (*s*)		1294 (*s*)		
	1486 (*sh*)		1286 (*sh*)	?	811 (*w*)
$Sm(NO_3)_3$	1506 (*sh*)		1296 (*s*)	?	814 (*w*)
	1501 (*s*)				
$Y(NO_3)_3$	1496 (*s*)		1281 (*s*)	?	811 (*w*)
$Sc(NO_3)_3$	1552 (*sh*)				
	1534 (*s*)		1285 (*s*)	?	806 (*w*)
	1516 (*sh*)				
$Th(NO_3)_4$	1538 (*s*)		1290 (*s*)	990 (*sh*)?	818 (*w*)
	1520 (*sh*)				
$Ce(NO_3)_4$ as	1531 (*s*)				
	1518 (*sh*)	1378 (*s*)	1270 (*s*)	?	806 (*w*)
$(NH_4)_2Ce(NO_3)_6$		1368, 1356 (*s*) (*s*)			
$UO_2(NO_3)_2$	1530 (*s*)	1400 (*sh*)	1271 (*s*)	990 (*sh*)?	835 (*m*)
	1520 (*sh*)	1375 (*s*)			808 (*w*)
Nitrates					
$La(NO_3)_3 \cdot 5H_2O^m$	1460 (*s*)		1331 (*s*)	1044 (*w*)	811 (*w*)
$Ce(NO_3)_3 \cdot 6H_2O^m$	1496 (*s*)		1361 (*sh*)	1036 (*w*)	804 (*s*)
	1454 (*s*)		1344 (*s*)		
			1314 (*s*)		
$Y(NO_3)_3 \cdot 3H_2O^{d,m}$	1495 (*s*)		1313 (*s*)	1028 (*w*)	802 (*w*)
$Sm(NO_3)_3 \cdot 6H_2O^m$	1471 (*s*)		1333 (*s*)	1031 (*s*)	806 (*w*)
$Sc(NO_3)_3 \cdot 4H_2O^m$	1511 (*s*)		1321 (*s*)	1036 (*w*)	804 (*w*)
$Th(NO_3)_4 \cdot 5H_2O^d$			1326 (*sh*)		
	1510 (*s*) Broad		1306 (*s*)	1023 (*m*)	796 (*w*)
$(NH_4)_2Ce(NO_3)_6^d$	1471 (*s*)		1360 (*sh*)		
	1406 (*sh*)		1331 (*sh*)	1036 (*w*)	808 (*w*)
	1388 (*vs*)				
$UO_2(NO_3)_2 \cdot 3H_2O^m$	1536 (*s*)		1346 (*s*)	1028 (*w*)	804 (*sh*)
	1510 (*sh*)		Broad		
CH_3ONO_2[17]	1672 (*vs*)		1287 (*s*)		759 (*m*)

Point group D_{3h}

	ν_3	ν_2
$NaNO_3$[88]	1368 (*vs*)	836 (*m*)
KNO_3[88]	1380 (*vs*)	824 (*m*)

(*vs* = very strong, *s* = strong, *sh* = shoulder, *m* = medium, *w* = weak)

The corresponding nitrate hydrates also demonstrate some splitting of the ν_3 frequency. However, in most cases no multiple bands are found. In addition the splitting for the TBP solvates is greater than that observed for the hydrates. Thus, in going from the nitrate hydrates to the nitrate TBP solvates a considerable decrease in symmetry of the nitrate group has occurred. Table 2 illustrates the degree of splitting which occurs in the compounds studied. The difference between the ν_4 and ν_1 frequencies may be taken as a measure of the dissymmetry arising in the nitrate group.

TABLE 2.—SPLITTING IN cm^{-1} OF VARIOUS TBP SOLVATES AND HYDRATES OF THE NITRATES OF THE TYPE $M(NO_3)_3$, $M(NO_3)_4$ AND $MO_2(NO_3)_2$

TBP solvate	Δ $(\nu_4 - \nu_1)$* (cm^{-1})	Hydrate	Δ $(\nu_4 - \nu_1)$* (cm^{-1})
$La(NO_3)_3$	193	$La(NO_3)_3 \cdot 5H_2O$	129
$Sm(NO_3)_3$	205	$Sm(NO_3)_3 \cdot 6H_2O$	138
$Sc(NO_3)_3$	246	$Sc(NO_3)_3 \cdot 4H_2O$	190
$Y(NO_3)_3$	215	$Y(NO_3)_3 \cdot 3H_2O$	182
$Ce(NO_3)_3$	207	$Ce(NO_3)_3 \cdot 6H_2O$	110
$Th(NO_3)_4$	248	$Th(NO_3)_4 \cdot 5H_2O$	204
$Ce(NO_3)_4$ as $(NH_4)_2Ce(NO_3)_6$	261	$Ce(NO_3)_4$ as $(NH_4)_2Ce(NO_3)_6$	141
$UO_2(NO_3)_2$	259	$UO_2(NO_3)_2 \cdot 3H_2O$	190
CH_3ONO_2	385		
		$NaNO_3$	0
		KNO_3	0

* Where multiple bands occur the most intense bands are used in obtaining this difference.

This will be designated as Δ, where $(\nu_4 - \nu_1) = \Delta$. It is observed that the Δ values for the TBP solvates are (193–261 cm^{-1}), whereas the hydrates show Δ values of (129–204 cm^{-1}). The Δ value for a covalently bonded nitrate such as CH_3ONO_2 is 385 cm^{-1} and that for an ionic nitrate ($NaNO_3$) is zero. It is thus concluded that the nitrate groups in the TBP solvates are not purely ionic, and have a higher degree of covalency than is found in the corresponding hydrates.

In the formation of the TBP solvates, the phosphoryl oxygen of the phosphate has been presumed to be involved in complex formation with the cation. This is supported by the evidence that the P → O frequency (~1275 cm^{-1} in TBP) is observed to shift toward lower frequencies. For trivalent cations, the shift is down to 1204–1216 cm^{-1}; for Th(IV), down to 1193 cm^{-1}; for Ce(IV), down to 1176 cm^{-1}; and for UO_2(II), down to 1179 cm^{-1}.

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STUDIES ON MONO- AND DI-*n*-BUTYLPHOSPHORIC ACIDS—I

THE SEPARATION OF MONO- AND DI-*n*-BUTYLPHOSPHORIC ACIDS BY SOLVENT EXTRACTION AND BY PAPER CHROMATOGRAPHY

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(*Received* 20 *October* 1958)

Abstract—The isolation of mono- and di-*n*-butylphosphoric acids from commercially available mixtures has been examined. A simple solvent extraction method based on the distribution of the acids between carbon tetrachloride–water, and diethylether–water, mixtures has been developed to obtain the individual acids with <1 per cent of total (<0·5 per cent acidic) impurities. A rapid paper chromatographic method of analysis is described which uses upward elution with a basic solvent mixture. The separated acids are then detected by spray reagents and the method allows approximately 0·5% v/v of each acid to be estimated visually in the presence of the other.

MONO- and di-alkylphosphoric acids are becoming increasingly used for the extraction of metals from aqueous solution, e.g. uranium,[1,2] protactinium,[3] zirconium and niobium,[4] yttrium,[5,6] and the lanthanides.[6] The mono- and di-*n*-butylphosphoric acids (H_2MBP and HDBP respectively) are of considerable importance in tributylphosphate (TBP) solvent extraction processes for separating uranium and plutonium from fission products.[7] These acids are produced in small amounts by the hydrolysis and radiolysis of TBP and form strong complexes with plutonium, zirconium, and niobium, which lead[8] to

(i) reduced decontamination of the uranium from the $\beta\gamma$-emitting zirconium and niobium, (ii) small but significant losses of uranium and plutonium, and (iii) contaminated solvents.

Mixtures of H_2MBP and HDBP are commercially available and we have examined the methods for their separation and purification and have developed simple solvent extraction methods to obtain the individual acids to a purity >99 per cent and a rapid paper-chromatographic method for their analysis.

METHODS FOR THE SEPARATION OF MIXTURES OF H_2MBP AND HDBP

The separation of mixtures of mono- and di-alkylphosphoric acids has been achieved up to the present by:

(i) multiple batch or counter-current extractions with immiscible organic and

(1) C. A. BLAKE, K. B. BROWN and C. F. COLEMAN, ORNL-1903 (1955).
(2) C. A. BLAKE, C. F. COLEMAN, K. B. BROWN, D. J. CROUSE and A. D. KELMERS, ORNL-2172 (1956).
(3) A. J. FUDGE and J. L. WOODHEAD, *Chem. & Ind.* 1122 (1957).
(4) E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
(5) D. DYRSSEN, *Acta Chem. Scand.* **11**, 1277 (1957).
(6) D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
(7) G. I. CATHERS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 490. United Nations (1956).
(8) P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. WAIN and J. L. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper 31, to be published, United Nations (1959).

aqueous phases,[9,10,11,12] e.g. dibutyl–ether and water, (ii) differential solubilities of the barium salts in water (the H_2MBP salt has the lower solubility), followed by repeated crystallization from aqueous alcoholic solution[13] and (iii) precipitation of ferric mono- and di-butylphosphates by the addition of ferric chloride solution, and partial separation of these by contact for 10 hr with a cation exchange resin; the ferric mono-butylphosphate dissolves and the remaining dibutylphosphate complex is decomposed with alkali and pure HDBP extracted from the solution.[14]

The above methods are either lengthy if products of high purity are required, or only give moderately pure H_2MBP, e.g. ~96 per cent,[11] which may not be sufficiently high for many applications. We have found that the method of KENNEDY and GRIMLEY[11] can be adapted to give a purity >99 per cent by a correct choice of the concentrations of H_2MBP and HDBP at each stage. The partition coefficients are markedly dependent upon the concentration of H_2MBP and HDBP due to deviations from ideality at these high concentrations, and the dimerisation of HDBP and the polymerization of H_2MBP in organic solvents.[15,16]

A typical commercial mixture of butylphosphoric acids (supplied by Albright and Wilson, Ltd., 49 Park Lane, London) contained[11] 40% w/w H_2MBP, 47% HDBP, 4% H_3PO_4, and 8–9 per cent of non-acidic impurities. Our procedure for the separation and purification of H_2MBP and HDBP from H_3PO_4 and the non-acidic impurities to yield colourless products is given below.

(i) *Separation of the* H_2MBP *and* HDBP

One volume of crude mixture is dissolved in four volumes of carbon tetrachloride and 98 per cent of the H_2MBP is extracted into 2 × 5 volumes of water by stirring the phases together for 2 min and combining the aqueous phases.

(ii) *Purification of* H_2MBP (*containing* ~10% HDBP)

The aqueous solution from (i) (approx. ten volumes) is washed with 10 × 2 volumes of CCl_4 (the first wash being retained for HDBP recovery and later washes discarded) and evaporated down to 2½ volumes under an infra-red lamp. The H_2MBP is extracted with 6 × 2½ volumes of diethylether, the ether phases are combined and washed with one volume of water. The water phases from these operations contain the H_3PO_4 and are discarded. The ether is removed on the water-pump and the H_2MBP finally vacuum-dried for 3–4 hr at 0·5 mm Hg and 50–70°C (water-bath).

The H_2MBP can be obtained as a crystalline solid (m.p. 24–25°C, density 1·24 gcm^{-3} at 20°C) by chilling the container for a few seconds in a bath of liquid air to initiate crystallization. The H_2MBP then slowly crystallizes and will remain solid at room temperature (20°C) whereas H_2MBP containing a few per cent of water or organic solvent remains a viscous liquid.

(iii) *Purification of* HDBP

The CCl_4 solution of HDBP from (i) together with the first CCl_4 wash from (ii) is treated with an excess (one volume) of 3 M NaOH solution in order to form the water-soluble sodium salt of HDBP. The alkaline solution is washed with 2 × 1 volume of CCl_4 (non-acidic solvent-soluble impurities are discarded with the CCl_4) and the aqueous phase is shaken for 20 min with a small quantity (0·1 g per 100 ml) of decolorizing charcoal, and filtered. The solution is then acidified with one volume of 4 N

[9] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).
[10] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[11] J. KENNEDY and S. S. GRIMLEY, AERE/CE/R-968 (1952).
[12] D. I. O. JOHNSON and G. L. MILWARD, CRL/A E-143 (1956).
[13] R. H. A. PLIMMER and W. J. N. BURCH, *J. Chem. Soc.* 292 (1929).
[14] E. CERRAI, C. CESARANO and F. GADDA, *Energia Nucleare* **4**, 405 (1957).
[15] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1771 (1957).
[16] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).

HNO_3 and the free HDBP extracted wtih 2 × 2 volumes of CCl_4. The CCl_4 phases are combined, treated with a small quantity of decolorizing charcoal, and filtered through a Whatman No. 42 filter paper. The CCl_4 solution (~4 volumes) is washed with 2 × 1 volume of 6 M HNO_3, 3 × 1 volume of water, and the CCl_4 is removed on the water pump at ~50°C. The HDBP is finally vacuum dried for 3–4 hr at 0·5 mm Hg and 70–80°C (water bath).

(iv) *Yield and purity determinations*

Chromatographic and electrometric methods. The paper-chromatographic method (described in detail later) was used to show that the H_2MBP and HDBP products contained <0·5% v/v of H_3PO_4 and of each other. Electrometric titration of the H_2MBP and HDBP products using a pH meter indicated a purity of 100 ± 1 per cent based on the theoretical molecular weights of 154·15 and 210·25 respectively.

Radiochemical method. The final separation and purification procedure was worked out by using radioactive $H_2MB^{32}P$ and $HDB^{32}P$ (obtained from the Radiochemical Centre, Amersham, Bucks, England). By separately adding $H_2MB^{32}P$ and $HDB^{32}P$ to the commercial mixture and processing this as described above for both H_2MBP and HDBP, 80% of the HDBP was recovered containing <0·2% H_2MBP, and 60% of the H_2MBP containing <0·5% HDBP. The concentration of HDBP and H_2MBP at each stage of the procedure was determined by β-counting samples in a standard 10 ml Geiger–Müller liquid counting tube, and applying appropriate corrections for paralysis time of counter, density of liquid, etc.

The distribution coefficient for H_2MBP between water and ether was in favour of the aqueous phase and increased as the concentration of H_2MBP increased. In order to obtain a good recovery it was necessary to evaporate the aqueous solution of H_2MBP to low bulk, but even so a loss of up to 35 per cent occurred, including about 15 per cent in the final water wash of the ether solution.

The loss of HDBP was much less due to the efficiency of the CCl_4 extractions, the distribution coefficient varying from about 40 for the first equal-volume water extraction of the initial CCl_4 solution, to about 15 for the final water wash before evaporation. In the first two water extractions of the CCl_4 solution 98 per cent of the H_2MBP was removed into the aqueous phase, and 94% of the HDBP retained in the CCl_4 phase.

THE CHROMATOGRAPHIC ANALYSIS OF MIXTURES OF H_2MBP, HDBP AND H_3PO_4

The separation of H_3PO_4, H_2MBP and HDBP by paper chromatography has been reported by CERRAI *et al.*[14] They obtained spots with R_f values of 0·11, 0·76 and 0·93 respectively by downward elution for 3 hr with a solvent mixture consisting of *n*-butanol, formic acid, and water (10 : 15 : 20 v/v). The substances were detected by spraying the paper either with brom-phenol blue indicator (yellow spots on a blue background) or with acid molybdate solution followed by hydrolysis of the esters and reduction of the phosphomolybdate complexes with H_2S (intense blue spots on a buff background). The method was successfully applied to the detection of these three phosphoric acids in the hydrolysis products of TBP.

A similar separation has been reported[17] as a method of chemical analysis used in the thorex solvent extraction process, but using a basic solvent mixture of ethanol–ammonia–water (60 : 30 : 10 w/w). The R_f values were (i) HDBP, a band across the strip at 0.90–0.92 and (ii) H_2MBP, a spot at 0·68 and a band at 0·48, but CERRAI *et al.*[14] attribute the latter band to H_3PO_4.

A simple method has now been developed for the separation of H_3PO_4, H_2MBP, and HDBP in about 30 min by upward elution with a solvent mixture consisting of equal parts by volume of *n*-butanol, acetone and 0·880 ammonia. Whatman No. 3 filter paper (type CRL) is used in the form of small sheets (21 cm × 11 cm) divided

[17] *KAPL Progress Report* 1477 (1956).

by slots into twelve strips (9 cm × 1·5 cm) on each of which a sample can be placed (Fig. 1). The sheet, in the form of a cylinder, is placed in a glass beaker (containing the solvent) which is covered with a Petri dish. The solvent mixture should be made up fresh, or used within a few hours, since it is apparently homogeneous for this length of time but later separates into two phases. It is not necessary to carefully pre-saturate the beaker with solvent vapour or to pre-treat the paper in any way; washing the paper with a solution of 8-hydroxyquinoline to remove metallic impurities had no effect upon the separation or quality of the spots. The paper should be eluted with

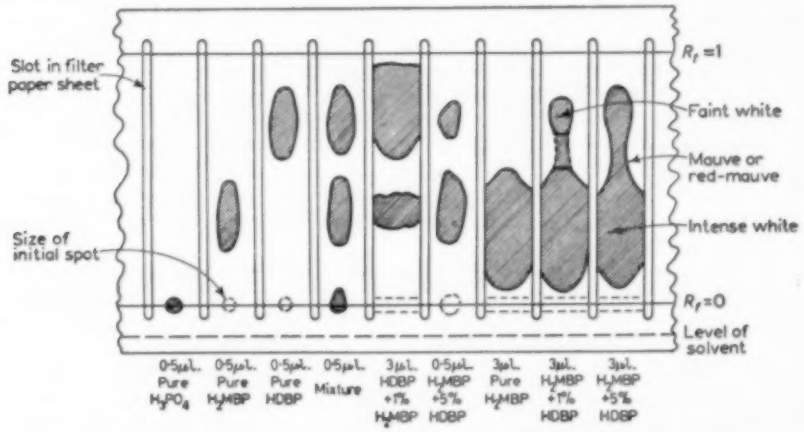

FIG. 1.—The paper-chromatographic separation of H_3PO_4, H_2MBP, and HDBP.

solvent as soon as possible after adding the samples, since the separation is impaired if the spots are allowed to dry. For the analysis of approximately equimolar amounts of H_2MBP and HDBP a 0·5–1 μl sample gives good separations, but when only a small percentage of one of the acids is present a 3–5 μl sample can be added as a band in order to show up the minor component.

After elution the strips are removed, dried with hot air from a hair-drier, sprayed with a 2% w/v solution of ferric chloride in 80 per cent alcohol, followed by 2% w/v sulphosalicylic acid in 80 per cent alcohol, and dried. White spots are obtained on a mauve or reddish-mauve background, due to the phosphoric acids complexing the ferric ions and the sulphosalicylic acid reacting with the free ferric ions to give a mauve complex.[18] Chromatograms are illustrated in Fig. 1 for samples of pure H_3PO_4, H_2MBP, HDBP and their mixtures. A small percentage of H_2MBP can be separated from a large sample (3 μl) of HDBP without any tailing between the bands, and approximately 0·5% v/v of H_2MBP impurity is just visible on a 3 μl sample with this method of detection (a chromatogram for 1% H_2MBP in HDBP is shown in Fig. 1). With a large sample (3 μl) of H_2MBP containing a small amount of HDBP the HDBP cannot usually be separated without serious tailing. However, by eluting a blank of the same volume of pure H_2MBP alongside the impure specimen, 1% v/v of HDBP can be clearly detected (compare the last three chromatograms in Fig. 1). The tailing is probably due to at least two effects, firstly the modification of the ascending solvent front by the large excess of H_2MBP, and secondly, by the association

[18] H. E. WADE and D. M. MORGAN, *Nature, Lond.* **171**, 530 (1953).

between H_2MBP and HDBP. A 0·5 μl sample of H_2MBP + 5% HDBP gives two spots with little tailing, whereas a 3 μl sample gives very bad tailing.

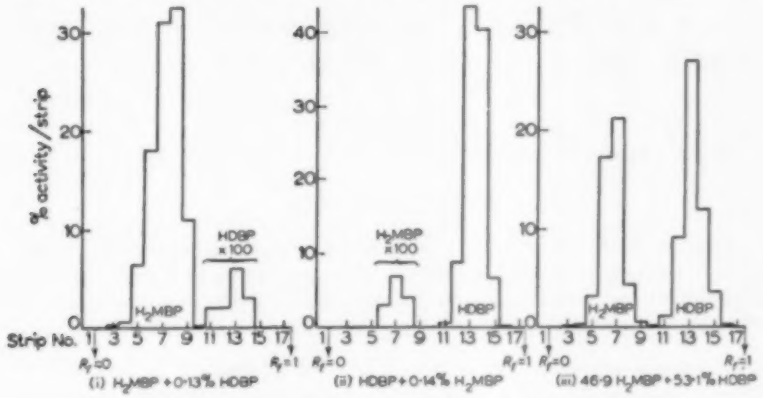

FIG. 2.—The separation of ^{32}P-labelled H_2MBP and HDBP.

The quality of the separation of the H_2MBP and HDBP has been checked with mixtures containing ^{32}P acids. The separation of 0·5 μl samples of

(i) $H_2MB^{32}P$ containing 0·1% $HDB^{32}P$,
(ii) $HDB^{32}P$ containing 0·1% $H_2MB^{32}P$, and
(iii) an approximately equimolar mixture, is shown in Fig. 2.

After elution the chromatogram was dried and cut into 17 × 5 mm strips and the β-activity emitted from the surface of each was counted with a standard Geiger tube in a lead castle. The count-rate was corrected for the paralysis time of the counter and the activity from each strip was expressed as a percentage of the total activity.

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STRESS RELAXATION AND EXCHANGE IN PELLETS USED FOR THE INFRA-RED TECHNIQUE*

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Abstract—In the pelleting of lead nitrates for infra-red study, exchange between lead nitrate and potassium chloride proceeds at a logarithmic rate. Water adsorption and stress relaxation also proceed at logarithmic rates. Increasing the rate of water adsorption enhances the rate of exchange and stress relaxation.

IN a study undertaken in this laboratory to study the interaction of NO_2 and metal oxides and of metal nitrates,[1] a troublesome interference occurred in employing the pelleting process used in the preparation of samples for infra-red studies. In the pelleting process it was found that certain characteristic bands appeared, while others disappeared. MELOCHE and KALBUS[2] in considering anomalies associated with the pelleting technique, has stated that exchange reactions were found to occur in many metal nitrates as evidenced by the 12·15 and 5·71 μ bands of potassium nitrate. He also stated that pressure applied during pelleting has the effect of shifting the 12·3–12·6 μ band of lead nitrate to 12 μ. MILLER and WILKINS[3] state that this shifting may be an orientation effect. BAKER[4] has made similar investigations; he states that after pellets are pressed they undergo a process of stress relaxation, which has the effect of reversing the pressure induced effects produced in the process of pelleting. The relaxation process is normally associated with a clouding of the pellet. In the investigations presented here, an attempt has been made to characterize the relaxation process and to follow the changes in lead nitrate as observed in its spectrum as a result of the pelleting process. A correlation of these processes with the presence of water is noted.

EXPERIMENTAL

The spectrum presented was obtained on a Model 21 Perkin–Elmer infra-red spectrometer. The samples were prepared by grinding and mixing in a vibrator (Wig-L-Bug). They were then pressed in an evacuated die at 20,000 lb in^{-2} in a Perkin–Elmer pellet die. The ultra-violet data presented were obtained on a Beckman automatic recording spectrophotometer. A special jig held the pelleted samples rigidly on position while the spectrum was taken.

RESULTS

The spectrum of a potassium chloride pellet containing ~1 per cent lead nitrate was taken in the Perkin–Elmer Model 21 spectrometer at various intervals. It was observed that when the pellets were evacuated for the prescribed period of 5 min and then pressed at 20,000 lb in^{-2}, the pellets retained their transparent qualities for long

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[1] F. VRATNY. To be published.
[2] V. W. MELOCHE and G. E. KALBUS, *J. Inorg. Nucl. Chem.* **6**, 104 (1958).
[3] F. A. MILLER and C. H. WILKINS, *Analyt. Chem.* **24**, 1253 (1952).
[4] A. V. BAKER, *J. Phys. Chem.* **61**, 450 (1957).

periods of time only if the humidity was relatively low. If the humidity was greater than about 70 per cent, or if the potassium chloride used in the preparation of the pellet had acquired a surface film of water which was not adequately removed in the process of evacuation, then the pellets were subject to a process of stress relaxation and exchange. Under these conditions, it was found that the background in the 2–6 μ region dropped, i.e. the transmittancy became less. With increasing time the bands at 3 and 6–14 μ grew in intensity when the humidity was significantly high. At the same time, two bands at 12·4 and 13·83 μ fell in intensity, without shifting, and

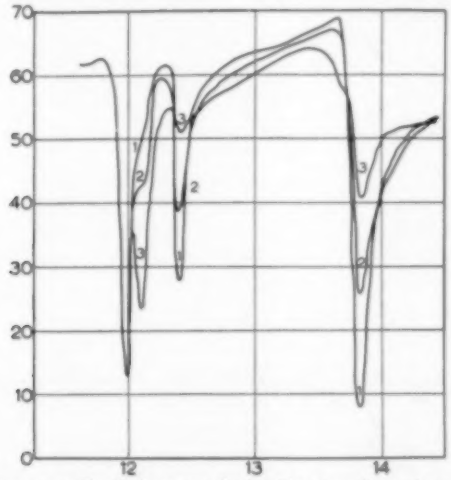

FIG. 1.—Infra-red spectra of lead nitrate as obtained by the pellet technique, for increasing age of the pellet (1–3), in the 12–14 μ region.

a new band appeared (and grew) at 12·1 μ. The general progression of the spectra in the 12–14 μ region is shown in Fig. 1. The change in transmittancy for the various bands are shown in Figs. 2, 3, 4 and 5.

Fig. 2 shows the decrease in transmittancy of the 13·83 μ band with time. This band has been correlated with the presence of lead nitrate.[1,4] Therefore a decrease in its intensity may be taken to signify a decrease in lead nitrate content. Three curves show the effect of humidity, and pumping time on this intensity decrease. At relatively low humidity (~60 per cent) the rate of decrease in intensity of this band is nearly zero; at elevated humidity 90 per cent the rate is greatly increased, and is further increased under higher humidity conditions. If potassium chloride is used in the preparation of a pellet which has acquired a surface film of water by standing in humid air, and if the pellet die is not evacuated for the requisite time, but only brought to a vacuum, exchange is noted to take place at rates approximating the 90 per cent humidity conditions while being observed in relatively dry air. Relatively short periods of pumping cause the rate of exchange to decrease very rapidly. A 2 min pumping period will reduce the rate to nearly that corresponding to the rate occurring for the 60 per cent humidity level. Shorter pumping times produced erratic results which yielded rates between these extremes. Fig. 3 shows the increase in intensity of the 12·12 μ band. This band has been correlated with the presence of potassium nitrate, by the author[1] and by MILLER and WILKINS;[3] therefore an increase in the intensity of this band may be taken to infer an increase in content of potassium

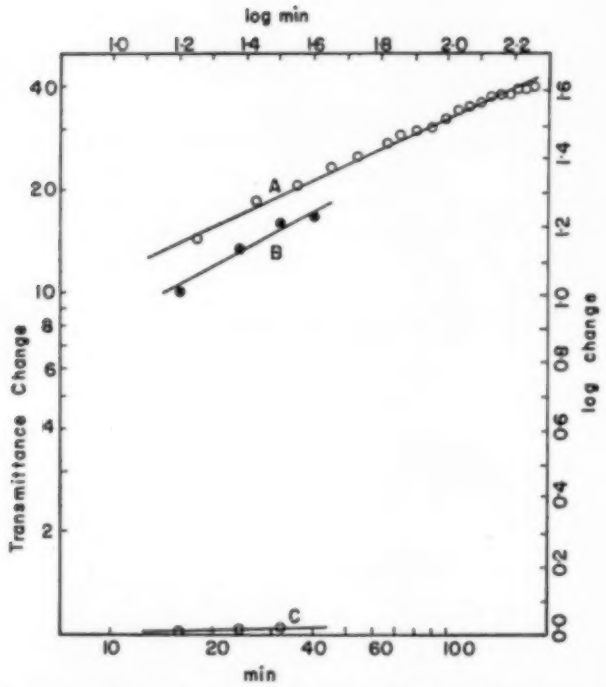

FIG. 2.—Change in the transmittancy of the 13·83 μ band of lead nitrate with increasing time; (A) for ~90 per cent humidity, (B) for short evacuation period, (C) for ~60 per cent humidity.

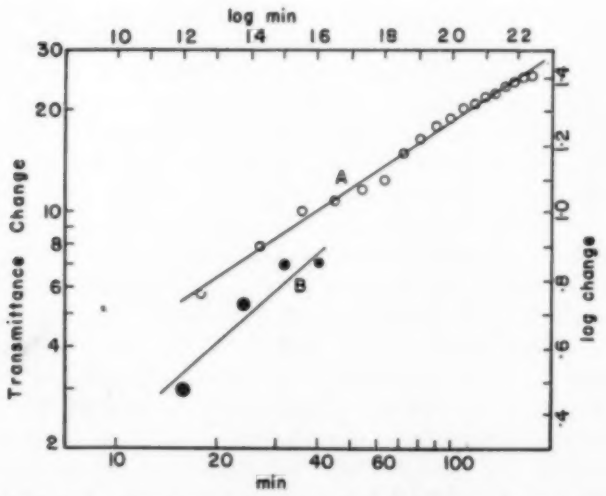

FIG. 3.—Change in the transmittancy of the 12·12 μ band with increasing time; (A) for ~90 per cent humidity, (B) for short evacuation period.

nitrate. Two rate curves are presented showing the effect of pumping and humidity. As above, for increased pumping time or lowered humidity the exchange rate drops nearly to zero.

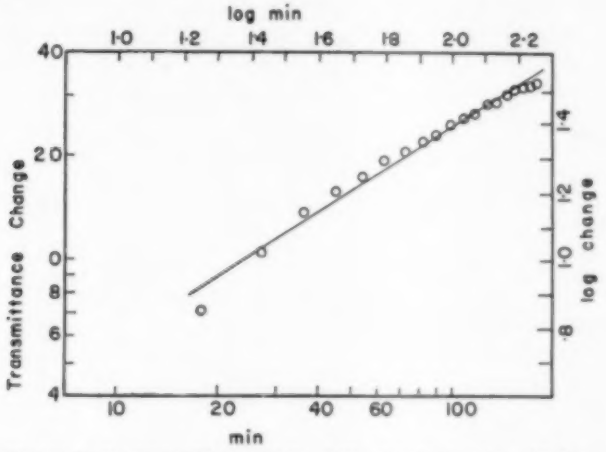

FIG. 4.—Change in the transmittancy of the 6·12 μ band of water with increasing time.

Fig. 4 shows the rate of change in the transmittancy of the 6·12 μ band, which has been associated with the presence of water.[5] Its growth infers adsorption of water from the air by the pellet. In relatively dry air this band remains constant in intensity. The phenomenon of water adsorption by pellets has been mentioned by many authors, in particular by BAKER.[4]

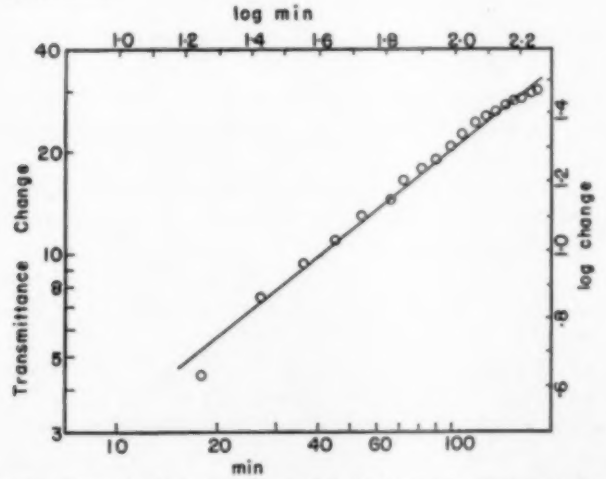

FIG. 5.—Change in the transmittancy of the background as measured at 5·5 μ.

Also mentioned above was the marked decrease in transmittancy in the 2–6 μ region. Fig. 5 shows the change in transmittancy as a function of time for an arbitrary wavelength (5·5 μ) on this background. This change in transmittancy has been taken to

[5] H. M. RANDALL, N. FUSON, R. G. FOWLER and J. R. DANGL, *Infrared Determination of Organic Structures*. Van Nostrand, New York (1949).

infer the occurrence of stress relaxation, associated with an increasing opaqueness of the pellet. In the process of stress relaxation the pellet breaks up into smaller units with the consequence of an increasing amount of scattered light from the multiple interfaces produced. With the increase in the amount of scattered light there is a resultant drop in transmittancy. In this instance, a decay was observed in the background as indicated in Fig. 4. In order to consider this matter further, the ultra-violet

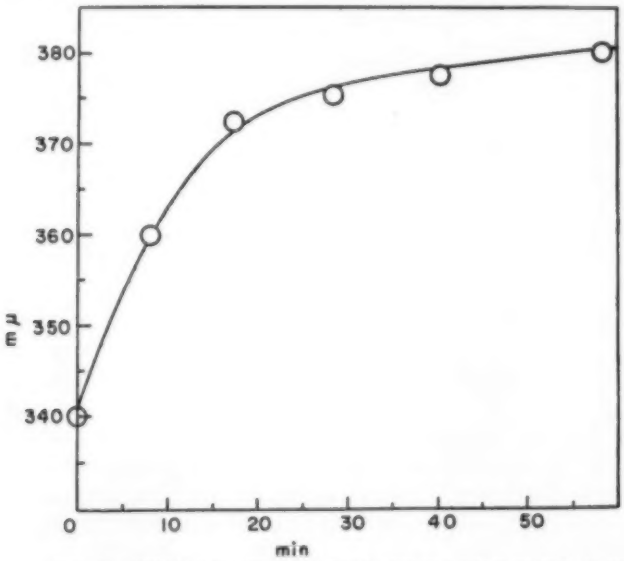

FIG. 6.—Shift in the ultra-violet band-edge of a pellet of CaF_2 in KCl.

spectrum of a pellet (CaF_2 in KCl) was studied. It was found that the absorption band edge of the pellet moved from the violet to the visible portion of the spectrum as a result of increasing amount of scattering and decreasing transmittancy. A plot of the movement of the band-edge as a function of time again gave rise to the curve shown in Fig. 6.

Stress relaxation was noted to take place as above in the case of exchange for both high humidity conditions and short pumping times. The rate of stress relaxation follows the above correlations.

CONCLUSIONS

Exchanges and stress relaxation proceed at rates controlled to a major extent by the humidity surrounding the pellet and evacuation time preceding pressing of the pellet. In relatively high humidity conditions (~90 per cent) exchange and stress relaxation are accomplished in a matter of hours. Similar rates are observed in damp potassium chloride, subjected to short periods of evacuation preceding the pressing of a pellet. For low humidity conditions, and relatively long periods of evacuation the rates of stress relaxation and exchange are brought essentially to zero. The variation in the ability of the pelleted material to adsorb water quite probably offers an explanation for the variability in the occurrence of exchange noticed by the author[1] and MELOCHE.[2]

Acknowledgement—The author wishes to express thanks to Dr. J. M. HONIG for his active support of this work.

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NOTES

The removal of traces of selenium from telluric acid by ion exchange

(*Received* 20 *February* 1959)

ANALYTICAL grade telluric acid contains a variable amount of selenium and figures between 3–70 p.p.m. have been obtained for different batches. It has been shown elsewhere[1] that selenium is present in both quadri- and hexavalent states, so that any method for purifying telluric acid must take into account both these forms.

As telluric acid ($K_1 = 1{\cdot}55 \times 10^{-8}$)[2] is considerably weaker than either selenious acid ($K_1 = 2{\cdot}7 \times 10^{-3}$)[3] or selenic acid ($K_1$ = ca. 10^{-2}),[4] an ion exchange separation was considered.

Telluric acid has been shown[5] to be only very slightly adsorbed on the chloride form of the strongly basic ion-exchange resin Amberlite IRA-400 from solutions of pH < 4·5. However, it has now been found that under these conditions adsorption of selenious acid is also low, and the acetate form of the resin is more suitable for the separation.

EXPERIMENTAL

Materials

A strongly basic anion-exchange resin, Amberlite IRA-400 analytical grade, was converted to the acetate form by treatment with 3 M sodium acetate solution, followed by extensive washing with deionized water.

Telluric acid was of analytical grade.

A solution of selenious acid was prepared from "Specpure" (Messrs. Johnson Matthey Ltd) selenium dioxide. Selenic acid of reagent grade was found to contain 1–2 per cent of quadrivalent selenium when analysed by the method of CHENG.[6] As this was objectionable, a solution of analytical grade sodium selenate acidified with the appropriate acid served as the source of selenate ions.

Analysis

(a) Tellurium was determined gravimetrically as the element following reduction with hydrazine dihydrochloride in 1·5–2·0 N hydrochloric acid solution.

(b) Quadrivalent selenium was followed by the use of ^{75}Se as radioactive tracer, prepared from selenium dioxide irradiated for 1 week at pile factor 10.

(c) Hexavalent selenium was also followed by the use of radioactive tracer. Analytical grade sodium selenate was irradiated for 4 weeks at pile factor 10, and held for 10 days before use to allow ^{24}Na (half life 15 hr) to decay.

RESULTS

Adsorption of tracer selenium from telluric acid solution on the acetate form of the resin

Quadrivalent selenium. To a solution of 10 g of telluric acid, 110 μg of tracer selenium was added as selenious acid. The solution was adjusted with acetic acid to pH 2·8, diluted to a volume of 500 ml, and passed at about 10 ml/hr through a column of resin 220 mm long and 5 mm diameter. The effluent and washings were evaporated to 25 ml (the limit imposed by the solubility of telluric acid),

[1] C. R. VEALE, *Analyst* To be published.
[2] F. FOUASSON, *Ann. Chim.* **3**, 594 (1948).
[3] E. BLANC, *J. Chim. Phys.* **18**, 40 (1920).
[4] R. W. GELBACH and G. B. KING, *J. Amer. Chem. Soc.* **64**, 1054 (1942).
[5] D. A. EVEREST and W. J. POPIEL, *J. Inorg. Nucl. Chem.* **6**, 153 (1958).
[6] K. L. CHENG, *Analyt. Chem.* **28**, 1738 (1956).

and no activity could be detected by liquid Geiger–Müller counting. The limit of detection at this volume was about 1·2 μg of selenium.

Hexavalent selenium. Under similar conditions 183 μg of hexavalent selenium as selenate added to a solution of 10 g of telluric acid gave rise to detectable activity equivalent to about 0·7 μg of selenium in the effluent plus washings.

Adsorption of tellurium from telluric acid solution on the acetate form of the resin

Since in the purification of telluric acid the amount of this passed per equivalent of resin would be large, the adsorption of tellurium was studied in the presence of much telluric acid. Varying amounts of telluric acid were passed through a column of resin which was then washed well with water; any adsorbed tellurium was eluted with 3 N hydrochloric acid and determined. Columns were 200 mm long × 5 mm dia. (Capacity 4·5 m eqiv); pH 3·0.

Millimoles of telluric acid solution passed	22	54	87	109
Concentration of telluric acid solution (molar)	0·087	0·217	0·348	0·435
Adsorbed tellurium, g atoms/equivalent of resin	5×10^{-5}	$1{\cdot}2 \times 10^{-3}$	$5{\cdot}6 \times 10^{-3}$	$7{\cdot}3 \times 10^{-3}$

Thus, using telluric acid solutions of less than 0·5 M, most of the resin is unaffected.

Ion exchange purification of telluric acid

The passage of telluric acid solution adjusted to pH 2·7–2·8 with acetic acid through a column of Amberlite IRA-400 resin in the acetate form has been used for the removal of selenium for several months. Using a colorimetric determination of selenium in telluric acid to be described elsewhere,[1] the effluent telluric acid has been found to contain consistently less than 0·2 p.p.m. of selenium when the starting material was analytical grade telluric acid with up to 70 p.p.m. of selenium.

Using telluric acid prepared from commercial tellurium by the method of HORNER and LEONARD,[7] the effluent has always contained less than 0·3 p.p.m. of selenium while the original telluric acid contained 10–40 p.p.m. of selenium.

Acknowledgements—The work described above has been carried out as part of the research programme of the National Chemical Laboratory, and this note is published by permission of the Director of the Laboratory.

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[7] H. J. HORNER and G. W. LEONARD, *J. Amer. Chem. Soc.* **74**, 3694 (1952).

Szilard–Chalmers effect of slow neutron capture in selenium dioxide

(*Received* 16 *March* 1959)

WE wish to report the results of preliminary experiments on the formation and possible enrichment of ^{75}Se (127 days) by the ^{74}Se$(n, \gamma)^{75}$Se reaction in solid selenium dioxide. The formation of ^{81}Se isomers by slow neutron irradiation of various selenium compounds has been studied by DAUDEL,[1] GUEST and EDWARDS[2] and APERS *et al.*[3] In each case a considerable fraction of the selenium activity could be separated either with or without a small amount of metallic selenium as carrier. The behaviour of induced ^{75}Se has not been checked under similar circumstances. If the long-lived activity could be similarly enriched it would be possible to improve the performance of radiographic sources using the low-energy γ-radiation from ^{75}Se.

[1] R. DAUDEL, *C. R. Acad. Sci., Paris* **214**, 547 (1942).
[2] H. GUEST and R. R. EDWARDS, Manhatten District Declassification Code Reports 1223 E (1947).
[3] D. J. APERS, P. C. CAPRON and L. J. GILLY, *J. Inorg. Nucl. Chem.* **5**, 2 (1957).

Selenium dioxide was purified by repeated sublimation. It was then sealed under vacuum in a silica ampoule and irradiated for one month at normal pile temperature in the reactor B.E.P.O., Harwell. The chemical treatment of the irradiated sample required careful standardization to obtain reproducible results. The final method chosen was as follows: Carrier selenium (red) was prepared immediately before use by adding 3 ml concentrated hydrochloric acid to 2 ml of a solution formed by the mixing of weighed amounts of selenium dioxide and sodium sulphite each dissolved in 1 ml water. Active selenium dioxide (about 20 mg) was dissolved in sodium hydroxide solution at such a pH that the solution remained alkaline after adding carrier. Red selenium metal was filtered off on

TABLE 1

Exp.	Activity of "free selenium" (counts/min)	Activity of "filtrate selenium" (counts/min)	Yield of "free selenium" (%)
1	109	24740	0·44
2	108	21970	0·49
3	121	20790	0·58
4	151	32540	0·46
5	97	17300	0·55
6	140	24400	0·57

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Whatman No. 42 paper after mixing for 1 min. The filtrate was then treated with barium chloride to separate barium selenite. The selenium and barium selenite fractions were counted in the solid state (on filter paper discs from a demountable filtration apparatus) by an end-window Geiger–Müller tube (EHM 2S). An aluminium absorber was used to remove conversion electrons and so diminish effects of self-absorption in the sample. Experimental results are shown in Table 1. The mean value of the percentage of ^{75}Se which was separable with red selenium carrier was 0·51 $\pm$ 0·07.

There was no detectable exchange between the two forms of selenium in alkaline solution in 2 hr. A check on a possible thermal relaxation of the crystalline material during activation in the pile was made to see if the low yield of "free selenium" could be explained in this way. A rigorous check, using ^{75}Se, was not feasible and the formation of ^{81}Se isomers was studied instead. Purified samples of selenium dioxide were activated in a paraffin block with a laboratory neutron source ($6·5 \times 10^6$ n/sec). The same chemical treatment as above was given to two samples, to one of them immediately after removal from the neutron source and to one of them after heating at 70°C for 105 min after removal from the source. The percentage "free selenium" yields for three experiments were 63, 78 and 68 (unheated samples) and 31, 36 and 35 (heated samples). The results as a whole show that there is a definite yield of ^{75}Se in lower-valence forms after slow neutron activation of solid selenium dioxide, that the yield after normal activation in the pile for a month is 0·5 per cent and that a thermal relaxation of the irradiated crystal is probably the cause of the low yields observed.

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LETTERS TO THE EDITOR

Tritium-labelled organic impurities in ^3He

(*Received* 25 *March* 1959)

TRITIUM is the primary radioactive isotope found as an impurity in commercial ^3He.* The chromatogram in Fig. 1 shows that tritium is found chemically bound, not only as hydrogen gas, but also as methane, ethane, propane, isobutane, *n*-butane, and with traces of higher hydrocarbons. The relative amounts of activity found in each chemical fraction are shown in Table 1. Similar activity ratios have been observed in several separate shipments of ^3He. There is no trace of any unsaturated hydrocarbon

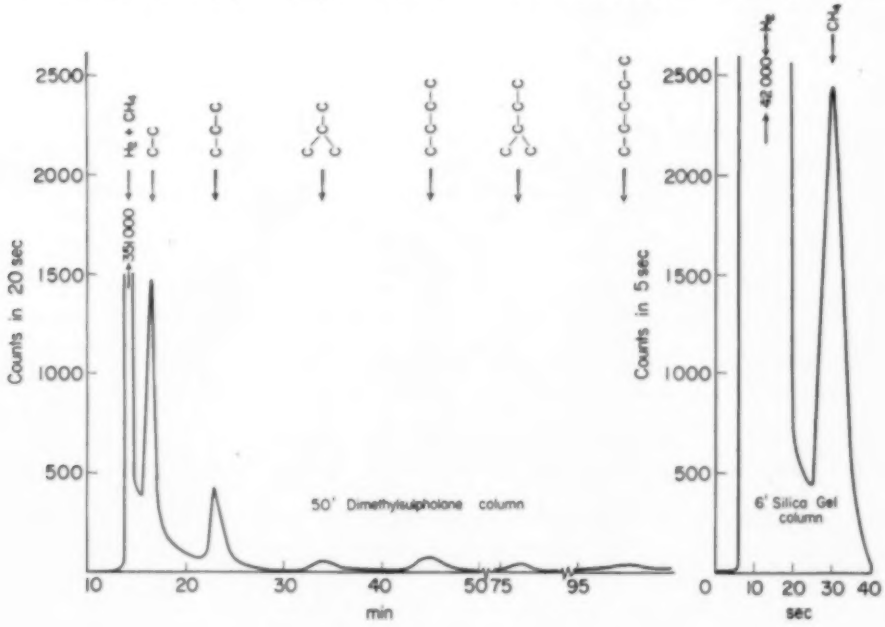

FIG. 1.—Tritium-labelled organic impurity in ^3He.

in the chromatogram. (Ethylene, acetylene, propylene, and the butenes would have been clearly distinguishable.) These organic impurities presumably come from radiation-chemical attack on trace carbon sources in the system.

The radioactive contaminants can be readily removed by several passes of the gas over CuO at 600°C and then through a liquid nitrogen trap. The same volume of ^3He after purification showed less than 100 counts in the hydrogen peak, and no detectable organic acitvity. The number of counts observed in the hydrogen peak corresponds to an impurity level of T_2 somewhat less than 1 part in 10^6, and is within the stated purity levels.

* As obtained from Oak Ridge National Laboratory.

EXPERIMENTAL

The separations were performed by standard gas chromatographic methods, using a 50 ft dimethylsulpholane column for one aliquot, and a 6 ft silica gel column for a second aliquot, both at 25°C. After the separation, using helium carrier gas, sufficient methane was introduced into the

TABLE 1.—CHEMICAL STATE OF TRITIUM IMPURITIES FOUND IN ^3He

Chemical state	Counts in peak		Tritium activity rel. to H_2
	D.M.S.	S.G.	
H_2	560,000	56000	1·0
CH_4		3340	6×10^{-2}
C_2H_6	2280	300	4×10^{-3}
C_3H_8	990	140	2×10^{-3}
i-C_4H_{10}	150		3×10^{-4}
n-C_4H_{10}	270		5×10^{-4}
i-C_5H_{12}	~30		6×10^{-5}
n-C_5H_{12}	~30		6×10^{-5}

flowing gas to permit proportional counting. The gas was then flowed through a proportional counter, and the number of counts recorded as a function of time. The identity of all peaks has been confirmed in separate experiments with macroscopic amounts of the organic gases.

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The extraction of cobalt(II) at tracer concentration from hydrochloric acid solutions into tri-*n*-butyl phosphate

(*Received* 7 *April* 1959)

IRVING and EDGINGTON[1] have recently investigated the extraction of some metal chlorides, including cobaltous chloride, into tri-*n*-butyl phosphate (TBP). We have independently studied the extraction of tracer cobalt (II) from hydrochloric acid solutions, and feel that our additional results may be of interest.

We have measured partition coefficients radiochemically using ^{60}Co as tracer and an initial aqueous phase cobalt concentration of $\sim 5 \times 10^{-7}$ M. The distribution experiments were performed with 10 ml of organic phase and 10 ml of aqueous phase, using the general technique of ALCOCK *et al.*[2] The ambient temperature was $19 \pm 1{\cdot}5°$. Equal volume aliquots of the phases separated after equilibration were transferred to polythene counting cells and counted directly with a NaI(Tl)

[1] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* In press.
[2] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).

γ-scintillation counter, type 1186A. Values for the (total) cobalt partition coefficient K were derived from the ratio of the counting rates (corrected for background) of the aliquots of the two phases.

Experimental results are given in Table 1. Hydrochloric acid concentrations in moles/l. are represented by the symbol c. Subscripts o and w refer to organic and aqueous phases respectively, and a superscript dash refers to a magnitude after equilibration. Our values of K in Table 1(a) correspond closely with those of IRVING and EDGINGTON,[1] and the results obtained for the distribution of hydrochloric acid between 100% TBP and water match those of PEPPARD *et al.*[3]

Log-log plots of K against concentration of TBP in benzene at constant c_w', Table 1(c), are straight lines of slope 2, indicating that 1 mole of the major cobalt species extracted is associated with 2 moles of TBP. Log-log plots of K for extraction by 100% TBP and 20% TBP in benzene against a_w' (thermodynamic activity of hydrochloric acid calculated from the data of HARNED and OWEN[4]) are straight lines of slope 2 for values of a_w' up to about 50. For this range of acidities therefore $(\partial \log K/\partial \log a_w')_{[Co]} = 2$. Similarly, for results with added NaCl, $(\partial \log K/\partial \log (a_{Cl^-})_w')_{[Co][H^+]} = 2$

TABLE 1.—EXTRACTION OF TRACER COBALT FROM HYDROCHLORIC ACID SOLUTIONS

(a) Extraction by 100% TBP from HCl + H_2O

c_w	K	c_o'	c_w'
1·10	0·0008	0·09	1·08
2·20	0·0015	0·23	2·12
2·30	0·0013	0·27	2·22
3·30	0·0054	0·44	2·88
4·40	0·020	0·89	3·96
4·60	0·021	1·01	4·17
5·50	0·054	1·27	4·84
6·60	0·169	1·66	5·74
7·70	0·450	1·97	6·36
8·05	0·776	2·27	7·20
8·80	1·09	2·36	7·44
9·20	1·29	2·63	7·98
10·35	1·50	2·95	8·90
	1·06	3·65	10·4

(b) Extraction by 20% (v/v) TBP in benzene from HCl + H_2O

c_w	K	c_o'	c_w'
3·48	0·0002(4)	0·01	3·55
4·64	0·0035	0·015	4·90
5·50	0·0056	0·04	5·36
6·60	0·0245	0·105	6·56
6·96	0·0339	0·11	6·80
7·70	0·122	0·18	7·50
8·80	0·212	0·32	8·54
9·90	0·164	0·44	9·48
10·44	0·138	0·49	9·85

[3] D. F. PEPPARD, G. W. MASON and J. L. MAIER, *J. Inorg. Nucl. Chem.* **3**, 215 (1956).
[4] H. S. HARNED and B. B. OWEN, *The Physical Chemistry of Electrolyte Solutions* (2nd Ed.). Reinhold, New York (1950).

(c) Effect of dilution of TBP with benzene at constant c_w'

$c_w' = 7{\cdot}83$		$c_w' = 9{\cdot}50$	
K	% TBP in benzene	K	% TBP in benzene
0·0011	2	0·0013	2
0·0022	3	0·0027	3
0·0033	4	0·0058	4
0·0060	5	0·0094	5
0·030	10		

(d) Extraction by 100% TBP from HCl + NaCl + H_2O

K	c_o'	c_w'	$(c_{NaCl})_w$
0·0033	0·30	1·98	1·0
0·010	0·445	1·98	2·0

These results suggest[5] that, for values of c_w' up to 4 M at least, the cobalt is extracted as $CoCl_2 \cdot 2TBP$ or $CoCl_2(H_2O)_2 \cdot 2TBP$.

We have also carried out some spectrophotometric studies with dilute solutions of cobalt, the results of which are summarized below.

Anhydrous cobaltous chloride dissolves in TBP to give a blue solution, the absorption spectrum of which shows two maxima at 580 and 662 mμ. When, however, the TBP contains hydrochloric acid (as is the case in extraction experiments), the solution is also blue but there are significant differences in the absorption spectrum. In the visible region, the absorption is characterized by three maxima at 625, 662 and 685 mμ respectively, and is closely similar to that shown by cobaltous chloride dissolved in strong aqueous hydrochloric acid.

KATZIN[6,7] attributed the absorption at ~690 mμ in acetone solutions containing cobaltous perchlorate and excess chloride, to the tetrachloro-complex ion, $CoCl_4^{2-}$. This absorption is also observed in the spectra of solids such as Cs_2CoCl_5 which have been shown to contain the $CoCl_4^{2-}$ ion,[8] although the ion does not survive in aqueous solution in the absence of additional Cl^-.

We conclude therefore that in the TBP extract from aqueous solutions containing cobalt and high concentrations of hydrochloric acid cobalt is present, at least partly, as the complex $CoCl_4^{2-}$—probably as the acido-complex $H_2CoCl_4 \cdot (2TBP)$. Application of JOB's method of continuous variations[9] to TBP solutions containing cobaltous chloride and hydrochloric acid provides evidence for the formation of such a complex, i.e. one in which the molecular ratio of the components HCl : $CoCl_2$ is 2 : 1.

We should like to thank Dr. H. IRVING for helpful discussion and Mr. D. N. EDGINGTON for permission to read his thesis.

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[5] H. IRVING, F. J. C. ROSSOTTI and R. J. P. WILLIAMS, *J. Chem. Soc.* 1906 (1955).
[6] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **72**, 5464 (1950).
[7] L. I. KATZIN, *J. Inorg. Nucl. Chem.* **4**, 187 (1957).
[8] H. M. POWELL and A. F. WELLS, *J. Chem. Soc.* 359 (1935).
[9] P. JOB, *Ann. Chim.* [10], **9**, 113 (1928).

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ANNOUNCEMENT

Russian Journal of Inorganic Chemistry

STARTING with the January, 1959 issue, The Chemical Society is to publish, with the support of the Department of Scientific and Industrial Research, a cover-to-cover translation of the monthly journal, *Zhurnal neorganicheskoi Khimii*, a publication of the Academy of Sciences of the U.S.S.R. The translation will be undertaken for the Society by Infosearch Ltd., and the Society has appointed Professor P. L. ROBINSON as Executive Editor of the publication. Professor ROBINSON will be assisted by an advisory panel of distinguished inorganic chemists.

The sale and distribution of the journal will be undertaken by Cleaver-Hume Press Ltd., 31 Wright's Lane, London W.8, from whom a detailed prospectus giving the scope of this journal may be obtained.

Translations will be issued in monthly parts as soon as possible after the Russian original is available. The subscription rate will be £30 (U.S.A. $90) per annum, but Universities and Technical Colleges may subscribe at a discount of 25%. Single issues can be purchased at £4 (U.S.A. $12) per copy to all purchasers.

The Society also hopes to start the publication within the next year of translations of the Russian *Journal of Physical Chemistry* (*Zhurnal fizicheskoi Khimii*) and *Progress in Chemistry* (*Uspekhi Khimii*).

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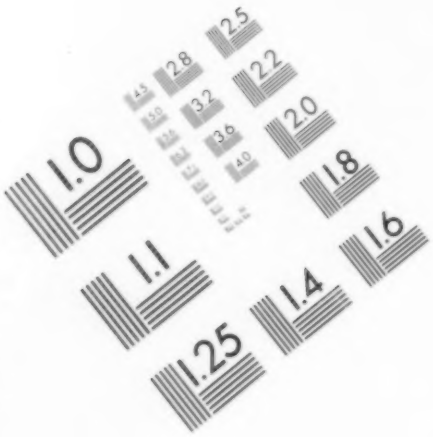

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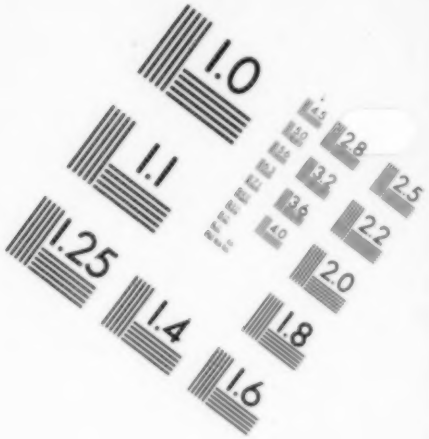

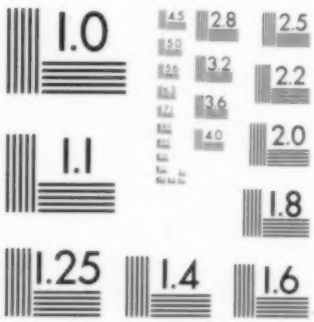

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